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In Silico Synthesis of Weakly Coordinating Anions

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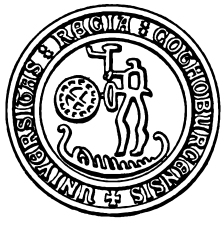

In Silico Synthesis of Weakly Coordinating Anions

Erik Abrahamsson

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Abstract

There is an enormous and continuously growing market for rechargeable batteries with high energy density and low environmental impact and the scientific and industrial *focii* are clearly directed towards rechargeable high energy density lithium batteries. A key component in these batteries is the electrolyte used, determining for example cyclability, safety and cost. The latter mainly due to the high price of the salts used in the electrolytes.

This master thesis aims at using computational chemistry as a tool to study new weakly coordinating anions to be used in polymer electrolytes, the most promising battery concept today. The weakly coordinating anions are studied by means of *ab initio* calculations. The same technique is further on used to study anion coordinating species and their interaction with various smaller, commonly used anions.

Several anions were studied, both derivatives of TFSI and new anions previously not synthesised. A number of anions with lithium affinities comparable to that of TFSI were synthesised *in silico*, as well as three anions with significantly lower lithium affinities. Of the studied anion coordinating species, two proved to be interesting. One calixpyrrole cryptand proved to have very high reaction energy with F^-, and one tetrahedral zwitterionic cryptand, with boron and nitrogen as ionic centres, showed high reaction energies with all the studied anions and formed complexes showing very low lithium affinity. It is now a challenge to inorganic chemists to synthesise the species and study them in polymer electrolytes.

Sammanfattning

Marknaden för laddningsbara batterier med hög energitäthet och låg miljöpåverkan är mycket stor och växter ständigt, och den vetenskapliga Det industriella intresset är idag fokuserat mot uppladdningsbara polymerbaserade litiumbatterier. En viktig beståndsdel i dessa batterier är elektrolyten, vilken bestämmer exempelvis livslängd, säkerhet och kostnad. Kostnaden i sin tur är starkt beroende av val av salt i elektrolyten.

I detta examensarbete används beräkningskemi som ett verktyg för att studera nya, svagt koordinerande anjoner, ämnade att användas i fasta polymerelektrolyter, elektrolyten i dagens mest lovande batterikonceptet. De svagt koordinerande anjonerna studeras med *ab initio*-beräkningar. Samma teknik utnyttjas för att studera anjon-koordinerande molekyler och deras interaktion med enkla och vanligt använda anjoner.

Ett flertal anjoner studerades, både derivat av TFSI och datorkonstruerade anjoner som ännu inte syntetiserats. Ett antal av de senare, d.v.s. anjoner som syntetiserats *in silico*, uppvisade litiumaffiniteter motsvarande den för TFSI, och tre av dem hade betydligt lägre litiumaffinitet än TFSI. Av de anjonkoordinerande molekylerna visade sig två vara lovande. En calixpyrrol-baserad kryptand uppvisade mycket hög reaktionsenergi med F^-, och en tetraedrisk zwitterjonisk kryptand, med bor och kväve som joncentra, uppvisade höga reaktionsenergier med alla de studerade anjonerna och anjonkomplexen uppvisade mycket låga litiumaffiniteter. Organiska och oorganiska kemister uppmanas nu att syntetisera dessa molekyler och anjoner och studera dem i polymerelektrolyter.

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Introduction

The rapid growth in concern over the global environment and the sudden awareness of limited natural resources has motivated worldwide research efforts to develop new technologies for the future electrical power generation and storage systems. Technologies based on electrochemical conversion and storage, like batteries and fuel cells, are in focus both for stationary use and for propulsion of electrical and hybrid cars. Another, less glorious but still very potent, driving force behind the development of new electrochemical conversion technologies is their use in small portable electronic devices like laptops, cellular phones and camcorders.

In the last two decades a new type of rechargeable, or secondary, lithium-batteries have received a large and still increasing interest from the research community. These new batteries are based on solid-state polymer electrolytes, SPE, formed by dissolution of a lithium-salt in suitable ion coordinating polymers. Since the potential of the reaction $Li \leftrightarrow Li^+ + e^-$ is large, and the lithium atom is light, batteries based on SPE have the potential to provide outstanding performance in terms of energy density, mechanical stability, and safety as compared with the conventional batteries based on liquid electrolytes [1,2,3]. Considerable research efforts have been directed to increase the performance of the electrolyte and to optimise the interface between the electrolyte and the electrodes. However, the SPE based batteries still cannot compete with combustion engines as power source in vehicles.

A technological breakthrough for the SPE based battery depends today to a large extent on an increase of the ion conducting ability of the polymer electrolyte. This can be achieved in many ways, and the focus of the research community has mainly been on modifications of the polymer itself, but also the choice of anion in the lithium salt will affect the ion conductivity of the polymer electrolyte. The choice of anion is, however, far from simple. The commonly used anion for research purposes today is TFSI, (bis(trifluoromethanesulphone)imide), but finding new anions, with weaker coordination of lithium, could drastically increase the ion conductivity of the polymer electrolyte.

In this study, *ab initio* calculation techniques are used to investigate two different approaches to increase the lithium ion conductivity in the polymer. Firstly, new anions are studied, both recently synthesised derivatives of TFSI and new anions, yet only existing on the computer. Their lithium binding energies are calculated, an

energy that should be as low as possible if the anion should be used in a lithium salt for a polymer electrolyte. Secondly, same technique is used to study the interaction of simple anions, like F^-, and ClO_4^-, with anion coordinating species. This way, the anionic charge is shielded, decreasing the lithium coordination of the anion, thus increasing the cation transport. The use of anion coordinating species in polymer electrolyte applications is a new idea, and few references of such research are found in the literature, making this study very interesting, as it might be breaking completely new ground.

Polymer Electrolytes

Ion conducting solid-state materials gained the attention of the research community in the late 1960s with the development of crystalline materials with high ionic mobility. During the oil crisis in early 1970s, the research in solid-state ion conductors increased, largely due to the increased focus on the development of heavy-duty batteries and fuel cells for electric vehicles. The field of solid-state ionics moved focus from crystalline materials to polymer electrolytes with Li^+ as charge carrier in the 1980s, though the high potential of the use of thin film polymers as electrolyte in an electrical cell was recognised by M. Armand in the early 1970s [2].

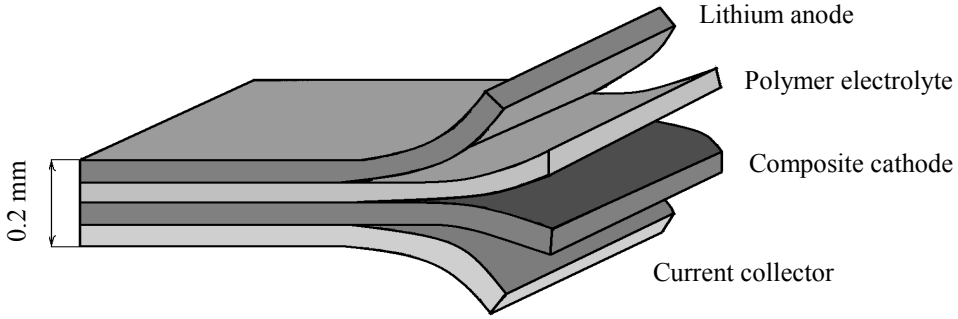


Figure 1. A lithium polymer battery

Ion conducting solid materials are usually divided in to four main groups; crystals, glass formers, molten salts, and polymer electrolytes; which all share great potential advantages over liquid electrolytes, the most obvious being the elimination of leaking of harmful substances. The solid-state electrochemical cells have a prospective of longer shelf life and higher energy density than their liquid counterparts. Especially polymer electrolytes with lithium ions as charge carriers are potentially very versatile, with applications ranging from miniaturised devices to electrical vehicles.

Solid-State Electrolytes

The first solid electrolytes studied were crystalline or glass forming, non-polymeric, solids, conducting a vast range of ions, both positively and negatively charged. The crystalline materials show a high concentration of mobile ions and low activation energy for transporting ions from site to site, resulting in a high ionic conductivity, even at ambient temperature. In the crystalline phase the ions move in a 1-, 2- or 3-dimensional network of channels, with large excess of available sites for the ions and high diffusion coefficients, resulting in a fast ionic transport. Glassy

electrolytes, in general, show lower conductivity than crystalline electrolytes, and the ionic transport is determined by diffusion, as in the liquid state. Both the crystalline and the glass forming solid electrolytes are hard and brittle materials, resulting in a low electrode contact, making them unsuitable for many applications.

Various molten alkali salts, such as eutectic mixtures of LiCl-KCl, show very high conductivities, but have the major drawbacks of a high operating temperature and very aggressive properties. Molten salts can also be used to increase the contact between the electrolyte and the electrodes in crystalline or glass cells.

The increasing scientific and industrial interest in polymer electrolytes have forced the development of several different types of ion conducting polymeric electrolytes, based on slightly different principles. Polymer electrolytes in the original sense are systems free of liquid solvents, where the polymer function both as charge separator, ion conductor, and solvent of the salt (figure 2(a)). In generally, these systems exhibit comparatively low ion conductivities, which has led to the development of gel electrolytes, where the polymer mainly function as stabiliser for a polar liquid solvent in which the salt is solvated. A plasticised electrolyte is a gel electrolyte with an ion conducting polymer and small amounts of a high dielectric constant solvent to increase the conductivity of the polymer. Other polymer electrolytes are ionic rubbers, which are molten salt mixtures, stabilised with small amounts of polymers, and membrane ionomers and proton conducting polyelectrolytes, polymers with ionising groups attached (figure 2(b)). The latter two electrolytes require a polar solvent or plasticiser to function, and are used in proton-exchange membrane fuel cells.

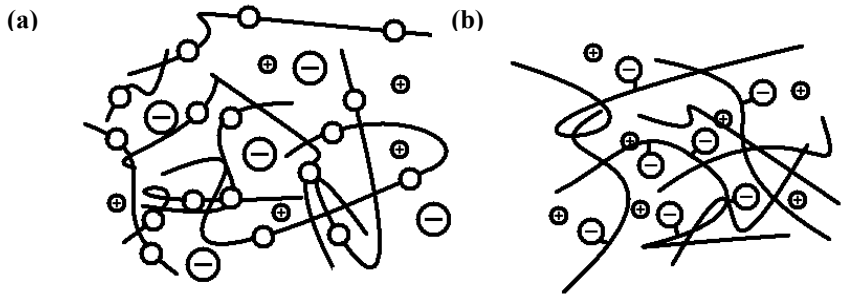


Figure 2. (a) Polymer electrolyte with cation coordinating sites (unfilled circles).
(b) Polyelectrolyte.
The polymer backbone is depicted as a solid line.

Requirements of the Polymer

A polymer suitable in a solid-state battery must have coordinating sites for one of the ions in the salt, competing with the counter-ion, in order to solvate the salts. If there are no such coordinating sites, such as in polyethylene, the salt cannot be solved into the polymer matrix. There are a number of problems associated with creating and using polymers with anion coordinating sites, such as complicated synthesis routes and increased rigidity of the matrix, resulting in increased glass transition temperature and decreased ionic transport. Thus, it is necessary to use polymers with cation coordinating sites, making *e.g.* polyesters and polyethers suitable as electrolytes. The coordinating sites should also be spaced so that the chain can wrap around the cation and coordinate it with more than one site without too much strain. For battery applications, the polymer must be electrochemically stable, with a voltage window wider than the voltage window of the electrode reactions, and sufficiently wide to accommodate any discharge or overcharging reactions. Thermal stability is also an important requirement of the polymer, as is mechanical stability, if the polymer should be suitable in a commercial product. The polymer must be electronically insulating and the resulting polymer electrolyte must have a sufficiently high ionic conductivity to allow reasonable current density for a practical application. The ion conductivity of crystalline or liquid electrolytes is up to thousand times that of the archetype polymer electrolytes, but a thin film polymer electrochemical cell configuration can compensate for the lower conductivity, reaching about 10^{-2} – 10^{-5} S cm^{-1} at room temperature [2,3]. The most commonly used polymer for lithium ion systems is poly(ethylene oxide) (PEO), -$(CH_2CH_2O)_n$-.

Ion Transport in Polymer Electrolytes

In a liquid electrolyte cell, the ion transport is determined by diffusion and Fick's law of diffusion holds. This is, to a first approximation also true for the plasticised polymer electrolytes. In a polymer electrolyte, however, the polymer not only functions as a mechanical stabiliser, but also as a solvent. The ions are not diffusing through the media, but randomly hopping from coordinating site to coordinating site located on the polymer. In the early days of polymer electrolyte research, it was assumed that the ions only were transported through tunnels formed by the crystalline polymers, wrapped up in helices. This view was proven wrong in the early 1980s,

when it was shown that ion conduction primarily occurs in the amorphous phase. The polymer chains are immobile on a macroscopic level, but short polymer sections are free to move about the C-C and O-C bonds, resulting in a constant forming and breaking of the bonds between the cations and the coordination sites on the polymer. The conductivity mechanisms are yet to be fully established, but a simplified view is interchain or intrachain hopping, with or without the aid of ion clusters. Figure 3(a) shows the case when the conduction of cations are achieved solely by segmental motion of the polymer, and in figure 3(b) the polymer acts as anchor points for ion clusters, where the cations move from cluster to cluster. Both of these mechanisms are possible to different extent, and which one is the dominating depends largely on the type and concentration of the salt, and the choice of polymer.

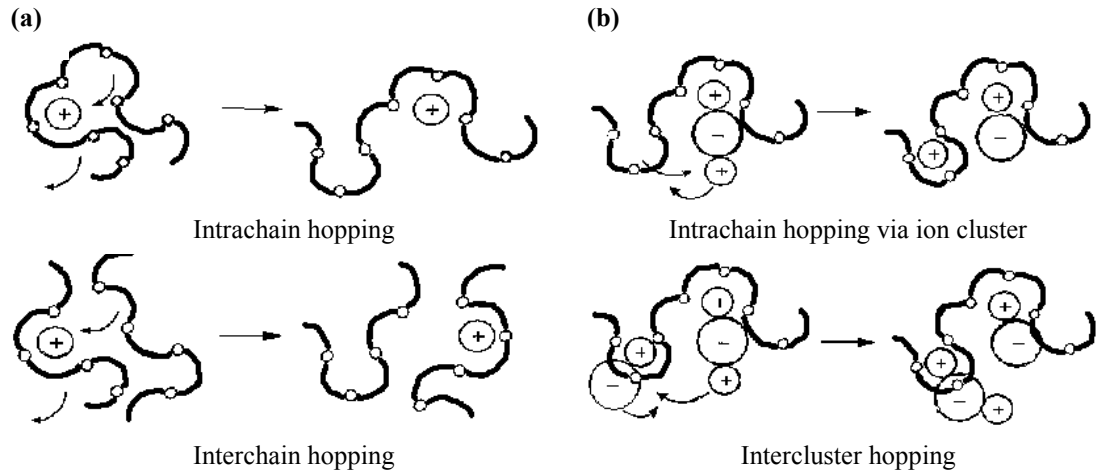


Figure 3. Representation of cation motion in a polymer electrolyte (a) assisted by polymer chain motion only; (b) taking account of ionic cluster contributions.

Solvation of the salt in the polymer depends on the cation-anion and the cation-polymer interaction, and the hard/soft acid base (HSAB) principle applies. Thus, PEO solves the hard lithium cation, as well as other alkaline and alkaline earth cations. To attain maximum solvation, the lattice energy of the salt should be as low as possible, *i.e.* lithium should be paired with soft bases, such as large, singly charged anions with delocalised charge, in order to minimise the lattice energy. Commonly used anions for experimental purposes are ClO_4^-, BF_4^- and triflate ($CF_3SO_3^-$). Recently a new anion, TFSI (bis(trifluoromethanesulphone)imide) ($N(CF_3SO_2)_2^-$) [9], has gained increased use, and an important and growing area in the field of polymer electrolytes is to find new, more weakly coordinating anions.

One other way of solvating salts in a polymer is to effectively remove the anions from the cations with anion coordinating species. By doing this, the salt is already solvated, and cation coordinating sites on the polymer are no longer needed to solvate the salt. Thus the cation will diffuse through the matrix without the requirement of forming and breaking polymer-cation bonds, increasing the ion conductivity. The field of anion coordinating macrocycles and cryptands is still in its infancy, and the use of anion coordinating complexes in polymer electrolytes is a very novel idea, that is yet to be explored.

Computational Quantum Chemistry

Chemistry by the Numbers

Modelling, simulations and calculations are important tools in all sciences, and chemistry is no exception. Just as in any other science, calculations can be used before experiments, to gain knowledge of what might be the expected result. More importantly, calculations can be used as a designer tool, a tool to explore the unknown.

Designing new molecules, created for a specific purpose, is an immense task, requiring a vast amount of guessing, thinking, experiments, failures and guessing again. Initial calculations can greatly simplify this work, as the molecules can be modelled before they exist in the real world. Calculations can predict the molecular properties, and an initial evaluation can be made before synthesis, thus eliminating the synthesis of many molecules that would prove to be unsuitable for their intended applications.

It is, however, important to remember that the calculations are no more than predictions and models. A calculated structure might not be stable in the real world or the actual reaction energy might differ from the calculated value, and that experiments are still needed to confirm the calculations. Still, calculations are just as powerful a tool in chemistry as in any other science, and computational chemistry is an ever increasingly important field of chemical research.

The computational techniques in focus in the present work are the Hartree-Fock methods, a group of relatively accurate and computationally cheep *ab initio* methods. Other *ab initio* methods are configuration interaction (CI), Møller-Plesset Perturbation Theory (MP), and Density Functional Theory (DFT), all with their specific advantages and disadvantages. The Hartree-Fock methods will be described in more detail below.

Ab Initio Calculations

Ab initio translates "from the beginning", emphasising that *ab initio* calculations are completely based on the laws of quantum mechanics. The mathematical treatment of quantum chemistry is very rigorous, and for practical reason, numerous simplifications are needed in order to calculate the wave functions for but the simplest molecules.

The Schrödinger Equation

The foundation of all quantum computational chemistry is the Schrödinger equation,

$$\left\{-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+V\right\}\Psi(r,t)=i\hbar\frac{\partial}{\partial t}\Psi(r,t) \qquad (1)$$

which describes the wave function $\Psi(r,t)$ of a particle moving in a potential V [4-8]. If the potential is independent of time, the Schrödinger equation can be separated into a time independent and a time dependent part:

$$\left\{-\frac{\hbar^2}{2m}\nabla^2+V\right\}\Psi(r)=E\Psi(r) \qquad (2)$$

$$T(t)=e^{-\frac{Et}{\hbar}} \qquad (3)$$

The time independent Schrödinger equation can only be solved analytically for the very simplest of atoms, the hydrogen atom. In order to solve for molecules, Born and Oppenheimer showed in 1927 that a very accurate approximation is to assume that the electrons are moving in the Coulomb field of fixed atomic nuclei. The kinetic energy of the electrons and nuclei can be considered separately. This separation of motion is based on the fact that the electrons are much lighter and faster than the nuclei, and reacts instantly to changes of the positions of the nuclei. The electronic wave functions Ψ_{el} are therefore given by

$$H_{el}\Psi_{el}(r) = E_{el}\Psi_{el}(r) \qquad (4)$$

with the Hamiltonian

$$H_{el}=\sum_i -\frac{\hbar^2}{2m}\nabla^2-\sum_i\sum_g\frac{Z_g e^2}{4\pi\varepsilon_0 r_{ig}}+\frac{1}{2}\sum_i\sum_j\frac{e^2}{4\pi\varepsilon_0 r_{ij}} \qquad (5)$$

where r_{ij} is the distance between electrons i and j, and r_{ig} is the distance between electron i and nucleus g. ε_0 is the electric constant and Z_g is the charge of atom g. The

calculated solution to equation (2) or (4) will be equal or higher than the true ground state energy E_0, a fact known as the variation principle.

The Hartree-Fock Approximation

Equation (4) can still not be solved analytically, since the Hamiltonian (equation (5)) contains an electron-electron repulsion term, which makes separation of variables impossible. This problem can be solved by replacing the two-electron term by an average repulsive field of all electrons in the molecule, known as the Hartree-Fock approximation. Equation (4) is then reduced to a set of coupled differential equations, each involving only one electron. Further simplifications are made by assuming that the electronic wave functions $\mathbf{\Psi}_i$ are linear combinations of basis functions ϕ_j

$$\Psi_i = \sum_j C_{ji}\phi_j \tag{6}$$

ϕ_j are often centred on the atoms, and are therefore called atomic orbitals, why the construction often is called linear combination of atomic orbitals (LCAO). The expansion coefficients C_i are called the molecular orbital coefficients.

The combination of the Hartree-Fock approximation and LCAO leads to the Roothaan-Hall matrix equations

$$\mathbf{FC}_i = E_i\mathbf{SC}_i \tag{7}$$

where $\mathbf{C}_i$ is a column vector, **F** is the Fock-operator, or Fock-matrix, equivalent to the Hamiltonian in the Schrödinger equation:

$$\mathbf{F} = -\frac{\hbar^2}{2m}\nabla^2 + V + J - K \tag{8}$$

where J is called the coulomb operator and represents the repulsion from all the electrons, including itself. This self-repulsion is compensated for by K, called the exchange operator. Finally, **S** is the matrix of overlap integrals

$$S_{ij} = \left\langle \phi_i^* \middle| \phi_j \right\rangle \tag{9}$$

The solutions to the Roothaan-Hall equation are found by an iterative procedure, known as self-consistent field (SCF), involving one-electron integrals $\left\langle \phi_i^* \middle| H \middle| \phi_j \right\rangle$ and a large number of two-electron integrals $\left\langle \phi_i^* \phi_j^* \middle| r_{12}^{-1} \middle| \phi_k \phi_l \right\rangle$ with four basis functions. The evaluation of these two-electron integrals is the most time consuming step for Hartree-Fock calculations. Hartree-Fock models are generally accurate methods for calculating geometries of molecules containing main-group elements and ground-state

conformations. The models are also useful for establishing conformational energy differences and reaction energies.

The limitations of the Hartree-Fock methods are failure to correctly estimate reactions involving explicit bond breaking and forming, and calculating geometries for molecules containing transition metals. This lack in the models can be ascribed to the replacement of two-electron interactions with an averaged field. Hartree-Fock methods are also time consuming. The computing cost formally scales as the fourth power of the number of basis functions used, but in practice, the cost scales as the cube of the number of basis functions used or lower. Hartree-Fock methods can today readily be applied to systems containing up to a hundred atoms or about 500 basis functions.

Gaussian Orbitals

There are a number of basis functions to choose from; one simple and accurate being the exponential functions, called Slater-type orbitals. Today, the commonly used basis functions are the Gaussian orbitals (figure 4), introduced independently by Boys and McWeeny in the 1960s. The Gaussian orbitals consist of one Cartesian polynomial and an exponential in r^2, $x^i y^j z^k \exp(-r^2)$. The great advantage of the Gaussian orbitals is that the product of two Gaussians can be expressed as a single Gaussian. The Gaussian orbitals resemble the exact solution of the orbitals for the hydrogen atom. Thus a Gaussian orbital of type $\exp(-r^2)$ is called an s-orbital; orbitals of type $x\exp(-r^2)$, $y\exp(-r^2)$ and $z\exp(-r^2)$ are called p-orbitals; and the six $x^2\exp(-r^2)$, $y^2\exp(-r^2)$, $z^2\exp(-r^2)$, $xy\exp(-r^2)$, $xz\exp(-r^2)$ and $yz\exp(-r^2)$ orbitals are called d-orbitals, even though formally, the orbital $(x^2+y^2+z^2)\exp(-r^2)$ is an s-orbital.

The major drawbacks of the Gaussian orbitals are their incorrect behaviour close to

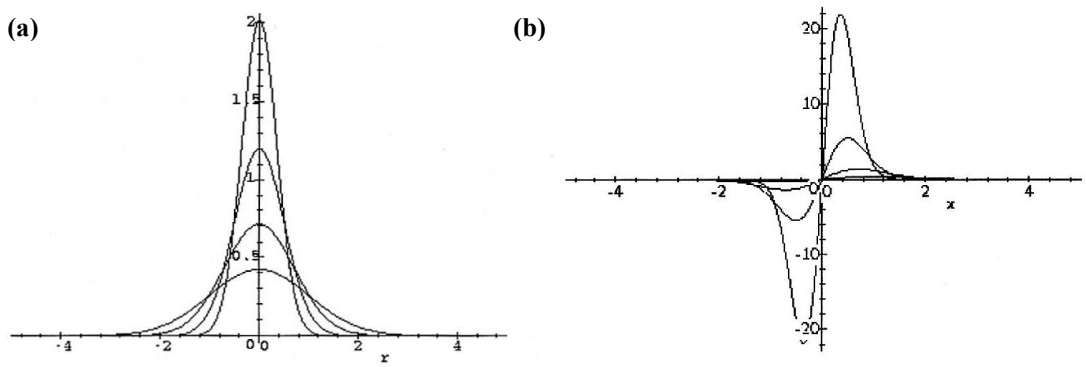


Figure 4. Normalised Gaussian functions. (a) s-type (b) p-type

zero and the fact that they die off too quickly with distance, forcing the use of more orbitals than are needed in the case of Slater-type orbitals.

Gaussian Basis Sets

A basis set containing only the functions necessary to accommodate the electrons of the atom is called a minimal basis set. Thus, a hydrogen atom or a helium atom is described by a single 1s-orbital while lithium to neon are described by two s-functions and three p-functions. STO-3G is a frequently used minimal basis set, representing each basis function with three Gaussians, with coefficients determined by least square best fit to Slater-type orbitals. The STO-3G basis set has spherical symmetry, making descriptions of atoms with non-spherical environment in a molecule inaccurate. Bonds between atoms are also inaccurately described by the STO-3G basis set since the basis functions are, by convention more than necessity, centred at the nuclei.

A basis set utilising twice the number of functions in a minimal basis set is called a double zeta basis set, while any basis set more refined than the minimal basis set is called an extended basis set. An example of an extended basis set is the split-valence basis sets, which splits the valence orbitals in two or more parts ("inner" and "outer" functions). For example, the hydrogen atom is described by two 1s-orbitals, while the carbon atom is described by one 1s-orbital, two 2s-orbitals and six 2p-orbitals. The splitting of the valance orbitals makes up for the minimal basis sets inability to accurately describe non-spherical atoms.

The number of Gaussians in the basis functions of the inner orbitals and the split valence orbitals classifies the split-valence basis sets. The inner orbitals of the simplest split-valence set, 3-21G, are represented by one function with three Gaussians, while the outer orbitals are split in two parts, written in terms of two and one Gaussians respectively. The 6-311G-basis set, called a triple split valence basis set, splits the valence orbitals in three parts, written in terms of three, one and one

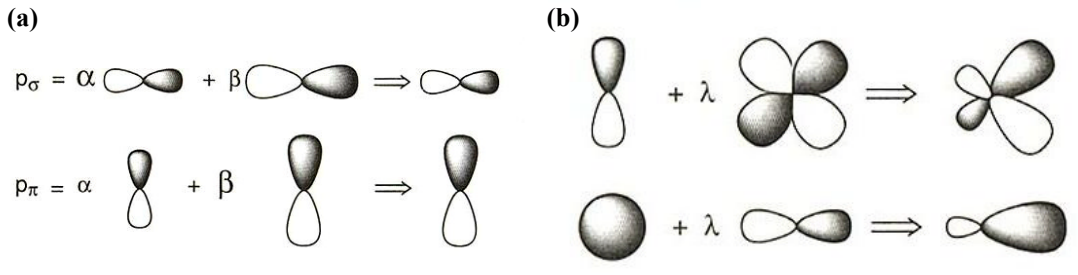


Figure 5. (a) Split valence basis sets. (b) Polarisation basis sets

Gaussian respectively, while the inner orbitals are represented by six Gaussians.

The split valance still cannot represent orbitals not centred at the nuclei, a problem solved by the polarisation basis sets. As in split valence basis sets, the polarisation basis sets represents the inner orbitals by one base function and the valence orbitals by two ore more base functions. The difference is the addition of six d-type functions to main-group atoms, allowing the centre of the electron distribution to be displaced from the nuclei. Common basis sets are 3-21G*, 6-31G* and 6-311G*, derived from 3-21G, 6-31G and 6-311G respectively. It is also possible to add p-type functions to hydrogen atoms in addition to the d-type functions to main-group elements, which is usually indicated by a double asterisk, *e.g.* 6-31G**.

Semi-Empirical Methods

Ab initio calculations are very computationally costly, and the cost increases quickly with the number of basis functions needed. By introducing further approximations and parameters based on experimental data, the computational cost might be decreased by several orders of magnitude. Semi-empirical models only consider the valence electrons, treating the inner-shell electrons as part of the nuclei, and uses minimal basis sets to describe the valence electrons. The most important approximation is the reduction of the overlap between orbitals centred on different nuclei to zero, entitled the neglect of diatomic differential overlap (NDDO) approximation.

The semi-empirical parameters are based on data from a large set of experiments, rendering data such as equilibrium geometries, dipole moments, and ionisation potentials. Semi-empirical models can be used to calculate equilibrium geometries for molecules with up to several thousand atoms. They are also reasonably accurate at calculating transition state geometries, but are not sufficiently accurate for thermochemical or kinetic calculations. The methods fail to accurately calculate hydrogen bonds and molecules with unusual bonds and situations, since there are no semi-empirical parameters for these cases. Semi-empirical methods can also be used as a first calculation step before continuing with *ab initio* models or to get qualitative information, such as vibrations and orbitals or general trends, such as conformational energy changes.

Pseudo Spectral Approach

Normally, all calculations are performed in the spectral space, spanned by the basis set. The software package Titan (Schrödinger, Inc./Wavefunction, Inc.) takes a different approach, called the pseudo spectral method [7]. Instead of calculating the integrals in the spectral space, Titan transfers the density matrix from the guessed wave function before all SCF iterations onto a grid spanned in physical space. The key integrals are evaluated on the grid and the operators for the Fock matrix are then transformed back to spectral space, where the wave function for the next iteration is generated. The pseudo spectral method is used for the majority of the two-electron integrals, but most of the one-electron integrals and some of the largest two-electron integrals are calculated analytically. The cost of transforming the wave functions to physical space is more than compensated for by the benefits done by calculating the integrals in physical space. By using both pseudo spectral and analytical methods Titan speeds up calculations, and can use coarser grids than normal numerical methods would need, without loosing accuracy.

Computations

Method

The computations within this project were performed with the software Titan 1.0.1 (Wavefunction Inc./Schrödinger Inc., Aug 16, 1999). In the Titan package, the interface from the molecular calculation software package Spartan (Wavefunction Inc.) is combined with the Jaguar (Schrödinger Inc.) algorithm, resulting in an easy to use and powerful tool for performing quantum chemistry calculations. The computations were made on a Dell Precision 330 equipped with a 1.4 GHz Pentium 4 processor. Due to the sizes of some of the molecules studied, a few calculations were performed at the Strindberg SP-2 at the Center for Parallel Computers (PDC), Royal Institute of Technology, Stockholm, using the Gaussian 98 package.

In this project, only the molecular properties in their optimised geometries are of interest. The geometries are optimised, with a few exceptions, by initially calculating the optimised geometry at the semi-empirical PM3 theory level, and then further refining at the HF level using the basis-sets, in order, 3-21G*, 6-31G*, and 6-311G*. The calculations result in the total electronic energy, the closed shell molecular orbital coefficients, the eigenvalues and the energies of the molecular orbitals, and the atomic charges from electrostatic potential, Mulliken population analysis, and natural atomic orbital populations. A number of electron density properties, such as HOMO (Highest Occupied Molecular Orbital), LUMO (Lowest Unoccupied Molecular Orbital) (figure 6) and charge density can also be calculated and displayed.

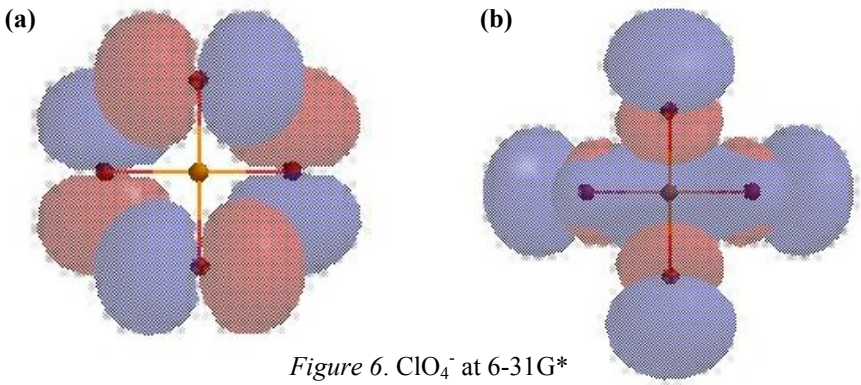


Figure 6. ClO_4^- at 6-31G*
(a) HOMO
(b) LUMO

Weakly Coordinating Anions

The ion conductivity in the polymer depends mainly on the properties of the two main components, the polymer and the salt. Most polymer electrolytes today are based on PEO, and there is intensive research on new PEO polymer derivatives with various structures, such as the addition of branches, interchain connections, and coordinating sites for both anions and cations. Since the solvation of the salt in the polymer depends mainly on the competition between the lithium coordinating sites on the polymer and the anion of the salt, the lattice energy of the salt, *i.e.* the coordinating strength of the anion, should be as low as possible, both to increase the solvation and to avoid formation of ion pairs in the solute. If the lattice energy is decreased, the coordinating sites on the polymer can be made weaker, increasing the diffusivity of the charge carrying cation.

Suitable anions should have largely delocalised charges, giving a low surface charge, such as large molecules with conjugated π-bonds. Incorporation of electron attracting groups, such as CF_3 and CN-groups further increase the charge dispersion. The anions should also be electrochemically stable in the voltage window of Li/Li^+, *i.e.* 0-4 V, and must be dissolvable in the polymer. There are a number of anions used in polymer electrolytes, *e.g.* ClO_4^-, BF_4^-, $CF_3SO_3^-$ (triflate) and TFSI, but to further increase ion conductivity of the system, finding new, even more weakly coordinating, anions is an important, but largely overlooked, area of research.

TFSI and Derivatives

The most promising anion used in lithium salts for polymer electrolyte research is TFSI, (bis(trifluoromethanesulphone)imide), $(CF_3SO_2)_2N^-$ (figure 7), which was first studied by Armand, Gorecki and Andréani [9]. TFSI has many great advantages over the other commonly used anions. The CF_3SO_2-group is one of the strongest electron

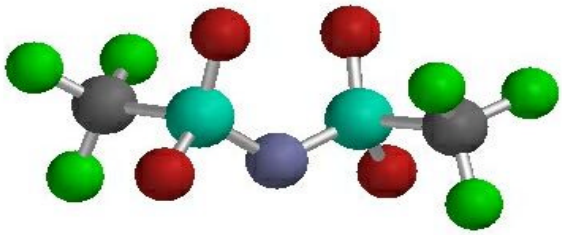


Figure 7. TFSI.

attractors known, effectively drawing electrons from the binding site at the centre of the imide-group, resulting in weak coordination of the cation and low solvation and lattice energy, which are the prerequisites for an anion to be used in a polymer electrolyte application. Furthermore, TFSI has a plasticising effect on the polymer, probably due to rotation about the two S-N bonds, resulting in increased ion conductivity, reaching around $5*10^{-5}$ S cm^{-1} for LiTFSI in PEO at room temperature.

The CF_3-groups on the TFSI molecules function as electron attractors, increasing the charge delocalisation. Thus, elongation of the CF-chain might further increase this effect, and decrease the reaction energy between the anion and the lithium cation.

This study aims at investigating the effects of elongation of the CF-chain on various properties of the anion and the anion-lithium-complex, such as the reaction energy of the reaction $An^- + Li^+ \leftrightarrow AnLi$, defined as

$$E_{bind} = E_{complex} - E_{Li+} - E_{anion} \tag{10}$$

the chemical hardness, defined as

$$\eta = \frac{E_{LUMO} - E_{HOMO}}{2} \tag{11}$$

which is a measure of the polarisability of the species, and the electron distribution in the different species. The study also aims at studying the calculation time as a function of the size of the molecule and to investigate how the choice of theory level affects the calculated properties of the molecules.

Discussion and Results

The optimised geometries were calculated for TFSI and six derivatives with extended CF-chains, named 5-FSI through 15-FSI. In order to have comparable results, the CF-chains on all TFSI derivatives were chosen to be non-branched. From previous calculations [10,11], it is known that the lithium ion binds non-covalently to two oxygen atoms located on each side of the central nitrogen. A typical anion-lithium complex, in this case 7-FSI - Li, is shown in figure 8. All molecules were constructed symmetrically, resulting in C_2 symmetry, both for the anions and for the anion-lithium complexes. This symmetry was forced during the calculations.

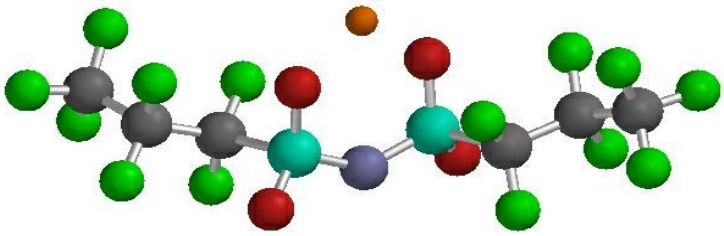


Figure 8. The 7-FSI-Li complex.

Comparing the different theory levels, *i.e.* the semi-empirical PM3 and the Hartree-Fock methods HF/3-21G*, HF/6-31G* and HF/6-311G*, it is seen that the PM3 level can be used only to investigate trends in reaction energy, since the calculated energies diverges a great amount from the results of the Hartree-Fock calculations, as shown in figure 9. Furthermore, it is seen that HF/6-31G* and HF/6-311G* gives approximately the same reaction energies, while the results of the HF/3-21G* calculations gives a higher reaction energy.

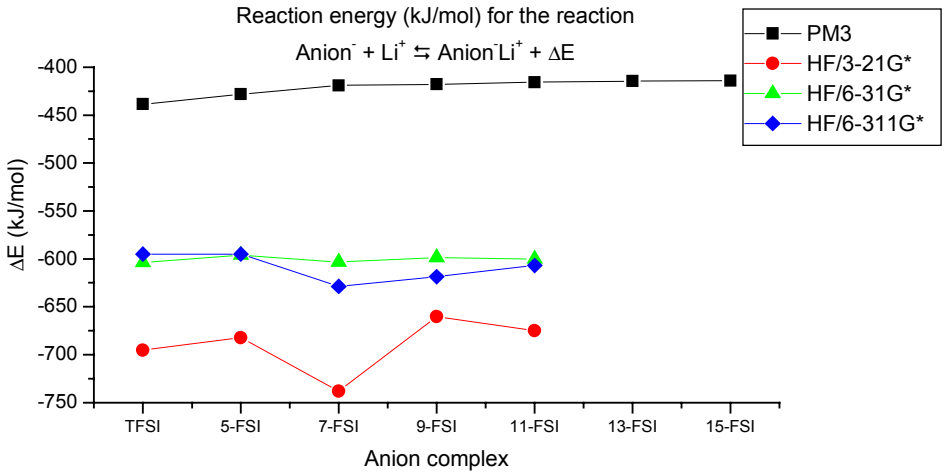


Figure 9. Li^+ binding energies of the TFSI derivates.

All four calculation methods result in comparable Mulliken charges, as seen in figure 10 for 9-FSI, which is a typical case (*c.f.* figure 13). All Hartree-Fock methods result in approximately the same chemical hardness, but the discrepancy with PM3 is large in the case of the anions (figure 11). However, the PM3 method gives a good starting point and significantly decreases the CPU-time used for further calculations, and gives reasonable optimised geometries. Thus, in order to achieve reliable results, *ab initio* methods, such as HF/6-31G* or HF/6-311G*, should be used after the initial PM3 calculations.

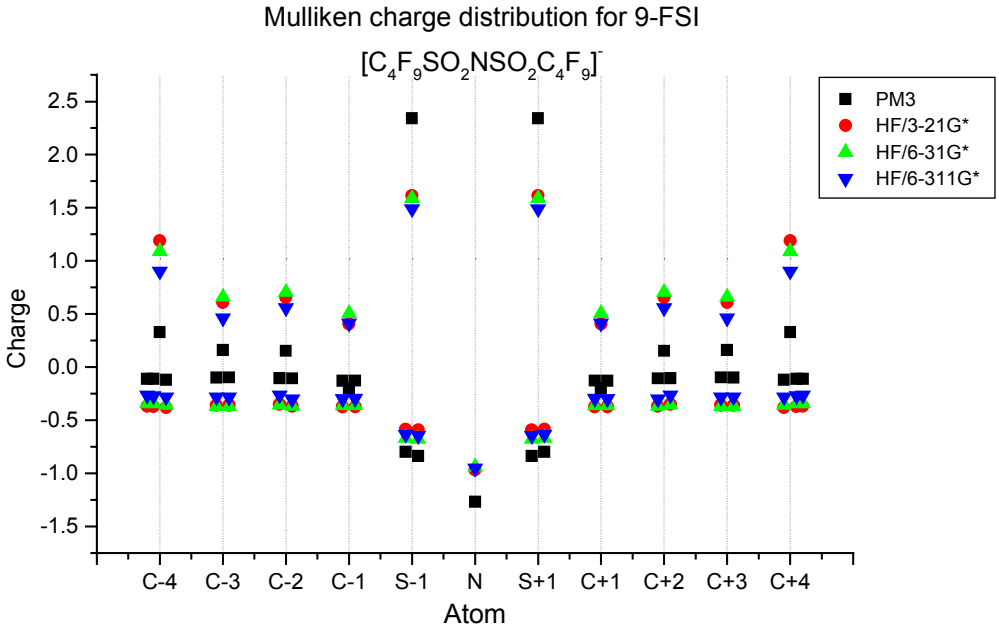


Figure 10. Mulliken charge distribution for 9-FSI.

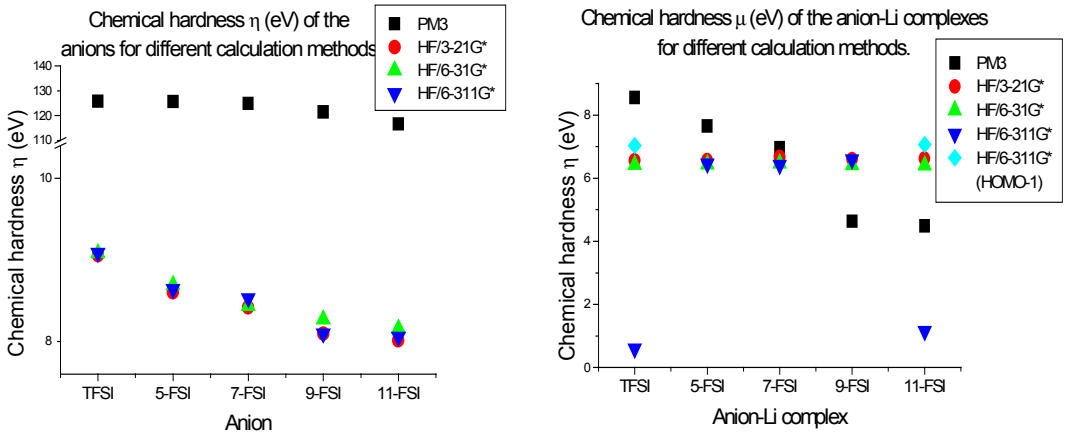


Figure 11. Chemical hardness of anion and anion-lithium complex.

In this study, the calculation time is found to increases approximately with the cube of the number of basis functions. It is also evident that the CPU-time consumption differs largely between the methods. For example, a PM3 calculation for 9-FSI requires 18 seconds, while the HF/6-31G* calculation for the same molecule takes almost 11 hours. A total CPU-time consumption of 60 hours allows for HF/6-311G* calculations to be made for molecules with around 800 basis functions, corresponding to approximately 300 electrons, on the computer used for these calculations.

However, this study is made on molecules with limited flexibility, due to the symmetry condition. Flexible and asymmetric molecules will most likely show increased CPU-times for the same number of heavy atoms, electrons and basis functions, compared to those in the TFSI derivative study.

As seen in figure 9 above, there is no evident change in the reaction energy as the CF-chains are extended. Nor is there any radical change in the Mulliken charge distribution (figure 12), for neither the anions nor the anion-lithium complexes as the chains are extended. The backbone carbon and sulphur atoms in figure 12 are labelled as in figure 13, with the oxygen and fluoride atoms plotted to the left and right of the carbon and sulphur respective.

The only obvious change between the species is the decreasing chemical hardness of the anions as the CF-chains are extended (see figure 11 above). The chemical hardness of the anion-lithium complexes remains essentially unchanged, which implies that the effect of the added lithium is stronger than the decreased chemical hardness of the anion. The sudden drop in hardness at HF/6-311G* for TFSI and 11-FSI, is most certainly due to calculation effects, since HOMO and LUMO is a purely mathematical construct. If the HOMO energy is replaced by the energy for HOMO-1, the chemical hardness for TFSI and 11-FSI at HF/6-311G*-level is consistent with the other calculations.

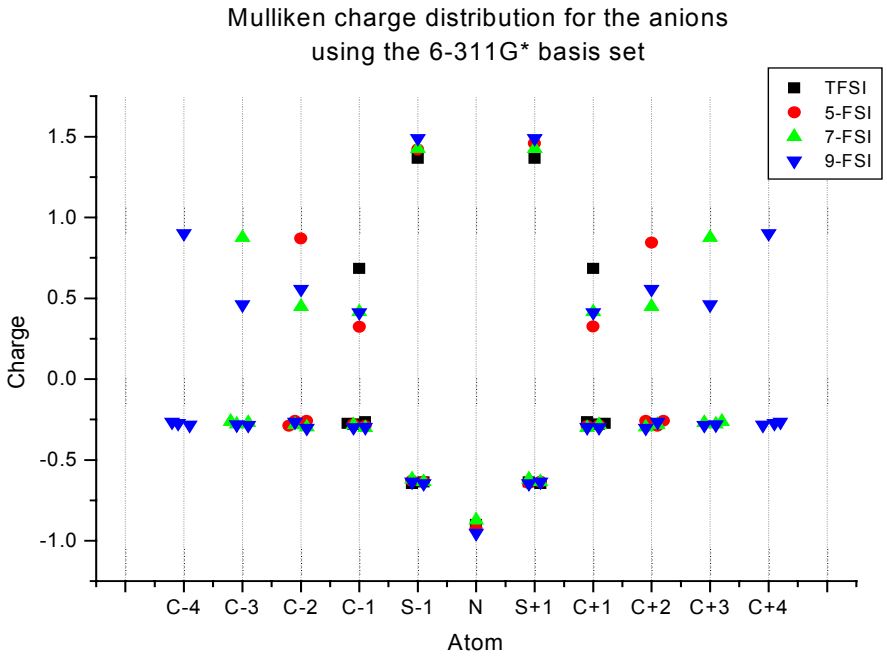


Figure 12. Charge distribution for the TFSI derivatives.

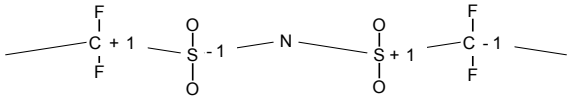


Figure 13. Numbering of atoms in figures 10 and 12.

The general conclusion that can be drawn from these calculations is that extension of the CF-chain in TFSI does not give any advantages over TFSI, based on reaction energy, charge distribution and chemical hardness. However, the extended FSI-species show no evidence of any disadvantages compared to TFSI, and no account is taken to the solvation in the polymer, plasticising effects, or effects at the electrodes. Thus, further studies might be of interest to show if extended FSI anions may be alternatives to TFSI in functional polymer electrolyte applications.

Finding New Weakly Coordinating Anions

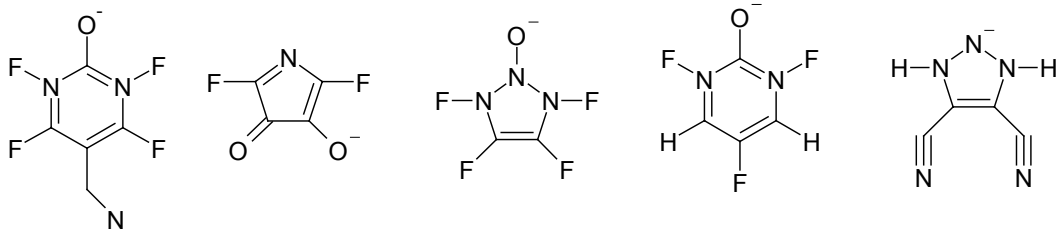
An anion replacing TFSI needs to either be more stable, more plasticising, cheaper, or bind more weakly to lithium than TFSI does. Finding new ions is an immense task, traditionally requiring a great amount of guessing, synthesising and experimenting. This study is an attempt to simplify the first steps of the process by making more or less initiated guesses of suitable anions, and calculate their reaction energies with lithium ions. If the calculated reaction energy is lower than the reaction energy of TFSI with lithium, the anion might be an alternative to TFSI and thus worth trying to synthesise. This does not guarantee that the anion actually will be better than TFSI in a polymer electrolyte application, but it does imply that this might be the case, and that further investigations are worthwhile.

The anions studied were based on nitrogen- and oxygen-substituted five- or six membered rings, with or without fluoride or cyanide as electron-drawing groups. Since the aim was to find new anions, the databases Chemfinder (CambridgeSoft) and Beilstein were searched for the anions. Only one reference, to the potassium salt of pentafluoro-phenol (**g**), could be found, indicating that none of the other anions have been synthesised.

Discussion and Results

A search for new materials like this must include a great number of failures, far more than the number of successes. In this case, a success is defined as finding an anion whose lithium binding energy is less than that of TFSI, *i.e.* around -600 kJ/mol at HF/6-311G*. In this study, however, a failure can also be a result, since the aim is to screen a number of anions as guidance as to which anions might have the right chemical properties for a polymer electrolyte application. Therefore, the anions exhibiting the largest exothermic reaction energies when reacting with lithium ions will first be presented, followed by the more successful cases.

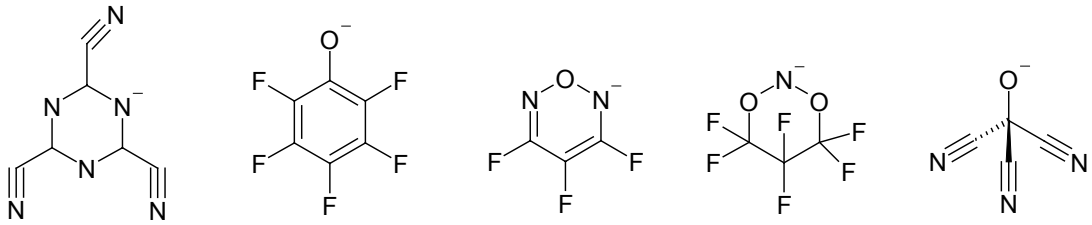
Figure 14 display five new anions with lithium binding energies, in descending order, between -926 and -672 kJ/mol at the HF/6-311G*-level. These anions are most likely not suitable as alternatives to TFSI, especially not **c**, which shows a tendency to be destabilised by lithium, forming new residues with a reaction energy of -650 kJ/mol.



a	**b**	**c**	**d**	**e**
$C_5F_4N_3O^-$	$C_4F_2NO_2^-$	$C_2F_4N_3O^-$	$C_4F_3H_2N_2O^-$	$C_4H_2N_5^-$
-925 kJ/mol	-858 kJ/mol	-702 kJ/mol	-693 kJ/mol	-672 kJ/mol

Figure 14. Anions **a**-**e**. Energies given at the HF/6-311G*-level.

The anions shown in figure 15 are considered more successful, as their respective lithium binding energies are in close proximity to that of TFSI, in particular **h** and **i**, both having a lithium binding energy of -612 kJ/mol and **j**, with a binding energy of -599 kJ/mol.



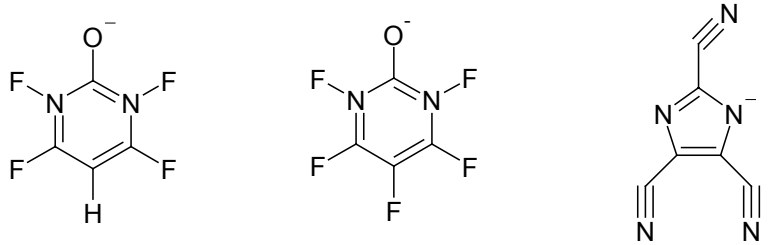
f	**g**	**h**	**i**	**j**
$C_6H_5N_6^-$	5-F-phenole$^-$	$C_3F_3N_2O^-$	$C_3F_6NO_2^-$	C4N3O$^-$
-642 kJ/mol	-634kJ/mol	-612kJ/mol	-612 kJ/mol	-599 kJ/mol

Figure 15. Anions **f**-**j**. Energies given at the HF/6-311G*-level.

Since these molecules have about the same lithium binding energies as TFSI, other properties, such as cost, synthesis, environmental impact, electrochemical stability and compatibility with polymers and electrodes, will determine whether any of them might be an alternative to TFSI. These anions now need to be investigated by organic and inorganic chemists. **g** is previously synthesised, and is thus interesting as it may be free of patent restrictions, which might make it cheaper than TFSI, and many of its

properties are already known. Still, investigations of the properties of **g** are needed before any conclusions can be drawn.

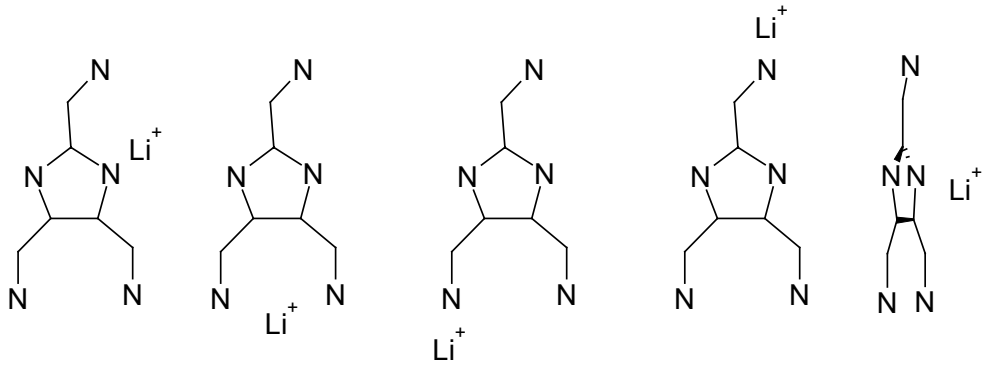
The two anions **k** and **l** (figure 16) have very low lithium binding energies, -539 kJ/mol respectively -524 kJ/mol, but they both show a tendency to be unstable, with a reaction energy with lithium of around –850 kJ/mol. In the case of **k**, the ring itself is broken up between one of the nitrogens and the adjacent carbon. **l** shows a tendency to loose a carbon-bound fluoride and result in the residues LiF + $C_4F_4N_2O$. However, such degradations might be avoided by adding groups with steric effects, or otherwise stabilising groups.



k	**l**	**m**
$C_4F_4HN_2O^-$	$C_4F_5N_2O^-$	$C_6N_5^-$
-539 kJ/mol	-524 kJ/mol	-486 kJ/mol

Figure 16. Anions **k**-**m**. Energies given at the HF/6-311G*-level.

Even lower energy is displayed by **m** (figure 16), having a maximum lithium binding energy at -486 kJ/mol, lowest of all anions encountered. **m** is found to have several stable binding sites for lithium, two around -485 kJ/mol and three around -440 kJ/mol, all but one in the plane of the ring (figure 17). The strongest coordination is found when the lithium is coordinated by one of the nitrogens in the ring, at a Li^+–N distance of 1.90 Å, which is longer than the Li^+–O distances of 1.83 Å in TFSI.



-486 kJ/mol	-480 kJ/mol	-443 kJ/mol	-441 kJ/mol	-434 kJ/mol

Figure 17. Li^+ binding sites at **m**. Energies given at the HF/6-311G*-level.

The Li^+–N distances in the other cases are 1.83 Å when lithium is coordinated by one nitrogen, and 2.03 Å and 2.20 Å in the cases where the lithium is coordinated by two nitrogens in or above the plane (figure 17(e)). This makes **m** a very interesting as alternative to TFSI, and the next step is now to synthesise **m** and study it in polymer electrolytes.

Of all the anions studied within this work, several has promising properties, especially **h** through to **m. m** is without doubt the most promising of them all, due to its low lithium binding energy, its many coordinating sites, and its seemingly simple structure. It is now a challenge to inorganic chemists to synthesise **m** and the other promising anions, and study their properties in polymer electrolytes.

Anion Coordinating Macromolecules

Most of the commonly used salts, especially LiTFSI, are rather expensive and harmful substances. Simple salts such as LiCl would naturally be much preferred, but due to the high lattice energies of such salts, they cannot be completely dissolved into the polymer. This can be solved by encapsulating the anion of the salt with a macrocycle or cryptand, coordinating the anion and effectively removing it from the cation. This means that with the right choice of macromolecule, any lithium salt can be used as charge carrier in the polymer electrolyte.

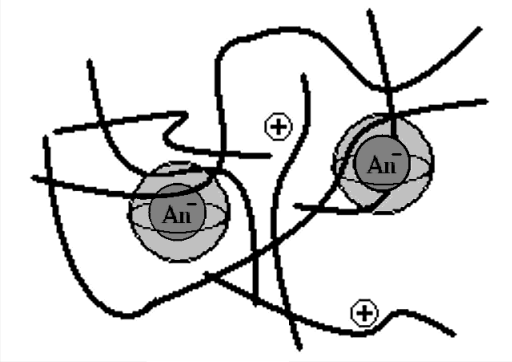


Figure 18. The concept of anion coordination in a polymer matrix.

The use of cryptands also has the additional effect that non-PEO polymers can be used in a polymer electrolyte, since the need for cation-coordinating sites on the polymer is largely reduced. Thus, the cation transport is increased, as the cations are moving more freely in the electrolyte. This could also be achieved by using an anion coordinating polymer matrix, but there are a number of problems associated with such polymers, for instance complicated synthesis routes and increased rigidity of the matrix. By using anion coordinating cryptands, these problems might be avoided.

Anion coordinating molecules is a rather recent area of research, as opposed to cation coordinating macrocycles, which have been studied since the late 1960's [12]. The main reason anion coordination has gained increased attention is mostly due to the increased knowledge about biochemical reactions and the increased need for more effective catalysts, and the main research focus is on anion recognition and anion coordination, not anion encapsulation. The macrocycles entered the area of polymer electrolyte research as cation coordinators in order to study the effect of different anions without the interference of the cations [13]. Recent studies have been made of macrocycles as a method of gaining more amorphous phase [14], and thus increasing

the ion conductivity. The use of anion coordinating macrocycles or cryptands as a method of solvating salts in non-PEO based polymer electrolytes is a novel idea that has not previously been reported.

This study aims at finding and investigating interesting macrocycles and cryptands, to be used in both PEO and non-PEO polymer electrolyte applications. Of interest are the reaction energy of the reaction *macromolecule* + *anion* ↔ *macromolecule-anion*, the reaction energy of *macromolecule-anion* + Li^+↔ *macromolecule-anion-Li,* and the physical encapsulation of the anionic charge in the cryptand or macrocycle. Recent molecular dynamics simulations of $LiPF_6$ and anion trapping aza ethers performed by Tasaki and Nakamura show that there is a direct correlation between this reaction energy and the increase of cation transport in the solvent [15].

Discussion and Results

Design of anion coordinating molecules is more problematic than the design of molecules coordinating cations. The anion is larger than the neutral molecule or the cation, resulting in lower charge to radius ratio and thus the electrostatic interactions with the coordinating molecule will be weaker. In this study, the aim is to remove the anions from the lithium cations, thus requiring the coordinating molecules to be neutrally charged, which introduces further complications.

The molecules investigated in this study (figure 19) are all but one (**19**) synthesised and known to coordinate various anions [12]. They have, however, not been studied by means of *ab initio* calculations or been considered as anion coordinators in a polymer electrolyte. The molecules were chosen because of their different configurations and methods of binding the anion. The numbering of the species in figure 19 follows that of Beer and Gale [12]. Molecule **3** is a neutral zwitterionic cryptand, forming a complex with the anion, binding it inside the cavity. Macrocycle **5** utilises three dipolar bonds to coordinate the anion below the ring, and is known to bind weakly with chloride and other anions in organic solvents. The macrocycles **6** and **18** and the molecule **16**, which strictly speaking isn't a macrocycle, are all known to bind anions through hydrogen bonds. The cryptand **19** has not previously been encountered in the literature.

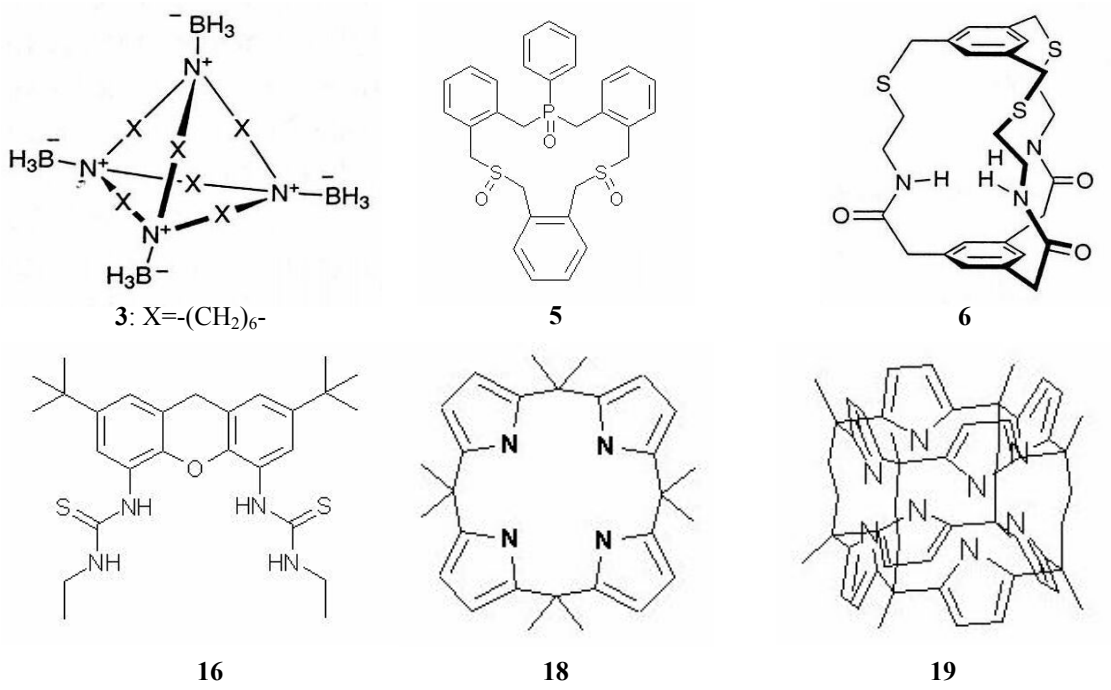


Figure 19. The studied anion coordinating species

The reaction energies of the reactions between the species and fluoride were first calculated and compared, and the encapsulation of the fluoride was studied by means of Mulliken charges and electron densities. The encapsulation of Cl^-, ClO_4^- and BF_4^- in macrocycle **3** and the coordination of Li^+ by the encapsulated anions were further investigated. The reactions between macrocycle **18** and LiF were also studied.

All the studied molecules show relative high reaction energies with F^- (figure 20), but still not as large as $LiF \leftrightarrow Li^+ + F^-$, except for **19**, making the encapsulation of the anion an increasingly important factor. Receptors **5**, **16** and **18** does not encapsulate

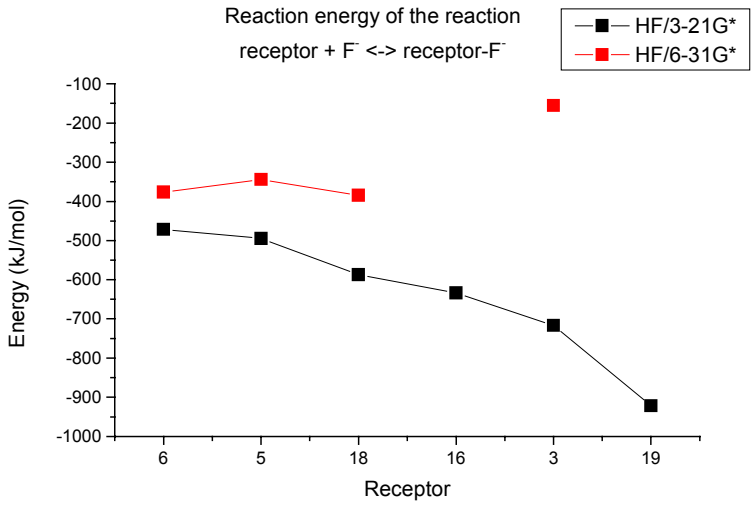


Figure 20. Reaction energies of coordinating species and F^-.

the fluoride, and **5** and **16** have strong negative centres that most likely will attract the lithium ion, making those molecules unlikely candidates as anion coordinators for electrochemical applications. Cryptands **3**, **6** and **19** encloses fluoride to a greater extent, but since **6** has three strong negative centres on the surface of the molecule, providing coordination sites for lithium ions, the cryptands **3** and **19** seem the most promising of the studied molecules.

Macrocycle **18** is a calix[4]pyrrole, a group of well-studied macrocycles based on pyrrole, known to coordinate anions. The reaction energy of the reaction between **18** and LiF was found to be moderate, around -550 kJ/mol at HF/3-21G*, which is lower

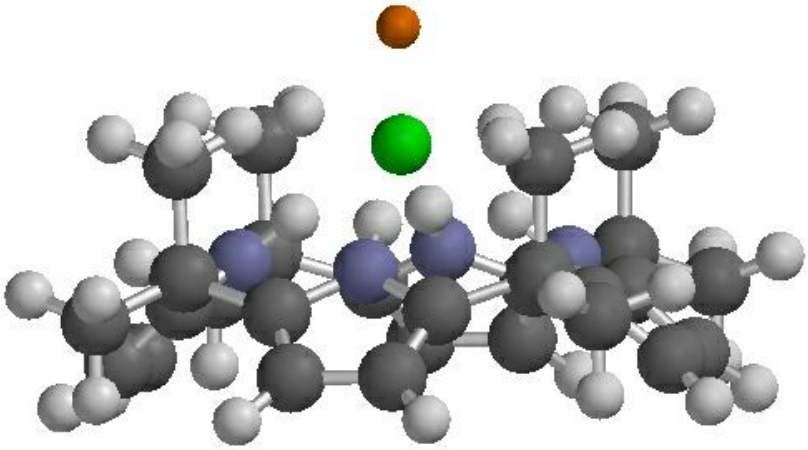


Figure 21. The **18**-F-Li complex.

than the lithium binding energy of TFSI (-695 kJ/mol at HF/3-21G*). This makes **18** interesting for a polymer electrolyte application, as it binds comparatively strongly to fluoride and does not stabilise ion pairs. The major drawback is the lack of encapsulation of the anion, which might indicate that the activation energy for removing the fluoride is low.

Cryptand **19** consists of two calix[4]pyrroles (**18**), forming a compact structure with a well-defined cavity. The first cryptand-like calixpyrrole, bicyclic[3,3,3]nonapyrrole, was not until very recently synthesised and shown to coordinate anions [16], but a cryptand such as **19** is still to be synthesised. The calculations of **19** at the HF/6-31G*-level were performed at Centre for Parallel Computers (PDC). The reaction energy of **19** with F^- (-922 kJ/mol at 3-21G*) is very large and in the vicinity of the reaction energy of LiF (-1037 kJ/mol at 3-21G*), indicating that **19** might successfully bind F^-, leaving Li^+ unattached. Due to the size of **19**, the 6-31G* calculations, performed at PDC, are still to converge, and more calculations at higher

level of theory are needed, as well as calculations such as the coordination of lithium to the **19**-anion complex, before further conclusions can be drawn. Calixpyrrole-based cryptands is a very interesting field of research and seem to be a very promising group of cryptands, well worth further investigations.

Further calculations were done on **3** with the anions F^-, Cl^-, ClO_4^- and BF_4^-, the HF/6-31G*-calculations of the latter two at the PDC. However, the calculations on the BF_4^- complex at PDC are still to converge. The reaction energies (figure 22) are significantly lower than the reaction energies of the respective salts. There is a large

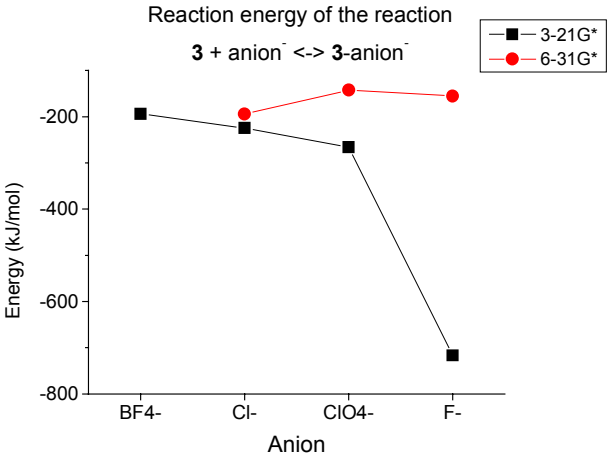


Figure 22. Reaction energies of **3** and anions.

discrepancy between the reaction energies of the reaction between **3** and F^- at the different calculation levels, due to a large conformational change between the two calculations. The cause for this difference in both energy and conformation is not known, but it might depend on an inability of the 3-21G*-basis set to accurately describe the electrostatic interactions between **3** and F^-. The reaction energy with ClO_4^- is the larger of the three (not counting F^-) at the HF/3-21G* level, but at HF/6-31G* Cl^- shows higher reaction energy. This is most likely due to the fact that mainly two factors affects the affinity of the anion; the delocalised charge, giving larger contribution to the reaction energy for Cl^-, and the contact with the walls of the cavity, which is larger for ClO_4^-. The results indicate that the delocalised charge is the main contributor to the binding of the anion. It would be a great advantage if LiCl could be used as salt, since it is cheap, easily purified and, contrary to ClO_4^-, not explosive in organic solvents.

The reaction energies of **3** with the various anions are in the range of -200 to -140 kJ/mol at HF/6-31G*, something that is far lower than the reaction energies

between the respective anions and lithium. However, these energies must still be considered as large, in the perspective that the anions have a very low charge to radius ratio compared to lithium. In this perspective, **3** effectively encapsulates the anions with sufficiently large binding energies to make it an interesting cryptand, possibly suitable for a polymer electrolyte application.

Further studies were made on the coordination of lithium by Cl^-, ClO_4^- and BF_4^- incorporated in **3** at HF/3-21G*. When an anion is incorporated into a cryptand like **3**, the complex can be seen as a large anion, which in turn coordinates the lithium cation. The calculated energies show that lithium is coordinated very weakly to the encapsulated ion, with binding energies far below those of the respective anions and the weakly coordinating anions used today; -481 kJ/mol in the case of **3**-Cl^- and -450 kJ/mol in the case of **3**-ClO_4^-. The BF_4^- once again proved to be a difficult species, as the calculation on the complex **3**-BF_4^--Li^+ is still to converge. The calculated Mulliken charges of the atoms in **3** confirm that the lithium ion will be coordinated by one of the oxygens on ClO_4^- and directly by the chloride anion in the case of Cl^-. The nitrogens on the corners of **3** draws electrons from the outside borons, which, in combinations with the hydrogens, makes **3** exhibit a positive surface, both inside the cavity and on the outside. This holds for both the neutral species and the complexes with the anions and anion-Li^+. These are all very promising results and strong indications that the usage of **3** will increase the cation conductivity in the polymer matrix. The next interesting study of **3** would be to investigate the effects of shortening the four CH_2-chains, to make a cavity volume closer to the volume of Cl^-.

Of the studied anion coordinating species, only two, the cryptands **3** and **19**, proved to be of any real interest for polymer electrolyte applications, both due to the encapsulation of the anions and the resulting reaction energies. Due to the size of **19**, it could not be investigated thoroughly and further calculations are called for. The calculations on **3** show that it has great potential for use in polymer electrolyte applications, as the complexes formed by **3** and the anions also show weak coordination of lithium, far weaker than the lithium coordination of the anions themselves. Most promising is the indication that **3** effectively encapsulates Cl^-, and the formed complex binds very weakly to Li^+. LiCl is a very cheap salt, and it would be a great benefit, both environmentally and economically, to escape synthesis involving fluoride chemistry. This makes **3** a very promising anion coordinator to use in polymer electrolytes.

Summary and Outlook

Computational quantum chemistry is a field of research that is growing every day, as the computational power increase. In this master thesis, computational chemistry is used as a tool to explore new methods of decreasing the lithium binding energy of anions used in polymer electrolytes, ultimately to be used in battery technology. New anions are explored, as well as the novel and fascinating idea of anion coordination, where simple and cheap anions like Cl^- and ClO_4^- are coordinated by a larger molecule, thus shielding the charge of the anions from the lithium.

The calculations of the commonly used TFSI-anion and extended FSI-anions showed no change in the reaction energy with lithium as the CF-chains were extended, nor did the Mulliken charge distribution change with the chain length. The only difference found, was a decrease in chemical hardness of the anions as the chains were extended. No obvious advantages with extended FSI-anions, compared to TFSI, can be found, implying that further studies, both in the laboratory and on the computer, are needed before any conclusions can be drawn. Only the lithium affinities were calculated in this study, and no account was taken to such properties as solvation in the polymer or effects at the electrodes.

Furthermore, several anions were synthesised *in silico*, *i.e.* constructed on the computer. Several anions (**f-j**, figure 15) with lithium binding energies near that of TFSI, -600 kJ/mol at HF/6-311G*, were found, as well as three anions (**k-m**, figure 16) with considerably lower binding energies, the most promising being **m**, with a maximum lithium binding energy as low as -486 kJ/mol. Further studies of the found anions, especially **m**, are now required, and the anions now need to be synthesised and studied in polymer electrolyte applications.

The studies on anion coordinating species resulted in two potentially interesting cryptands, **3**, synthesised by Schmidtchen [12] and **19**, not encountered in the literature. **19** is a very large molecule, making *ab initio* calculations very costly, and the calculations at the HF/6-31G* level, performed at PDC, are still to converge. The cryptand has potential to effective encapsulate small anions, but further calculations are needed. The zwitterion **3** was found to be a very promising cryptand, as it effectively enclosed the studied anions with sufficiently high energy, between -200 and -140 kJ/mol, to keep the anions enclosed in the cavity. Computations on the complexes formed by **3** and the anions Cl^- and ClO_4^- with lithium showed that the

coordination of Li^+ is very weak, -481 and -450 kJ/mol respectively. These calculations now needs to be refined at higher levels before **3** is ready to take the step out of the computer and into the polymer electrolyte.

The Future

The environmental benefits of more effective batteries cannot be overestimated. Combustion of fossil fuels, especially for transportation purposes, is the main source of greenhouse and nitrous gases [17], some of the great threats to our environment, as well as other harmful gases and particles. Powerful, long life battery packs for electrical vehicles, competing with combustion engines, will without doubt contribute to a decrease in the pollution of our world. Effective, miniaturised batteries, used in small portable electrical devices, will also increase our mobility and communication possibilities, increasing our quality of life. Batteries utilising polymer electrolytes as conductors of lithium ions is today the most versatile and promising battery technology, with several advantages over the liquid electrolytes. Still, polymer electrolytes do not have sufficiently high ion conductivity to be a commercial alternative to other power sources. However, these problems are not insurmountable, and in the race to solve the remaining issues, computational chemistry will be a powerful tool, a tool that might help saving our world.

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