Final Report: First Principles Hierarchical Selection and Testing of Anion Receptors for High Specific Energy Lithium-Fluoride Batteries
JPL Task Plan 81-11600

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<u>**Executive Summary**</u>
New anion receptors have been designed, modeled, synthesized, and tested at the battery cell level for use in dual ion intercalating batteries. In particular, a promising new class of cyclic fluorophenyl boronic acid anhydride (fluorophenyl boroxine) anion receptors was identified. The binding energetics of these compounds to fluoride can be readily varied by tailoring the degree of fluorination on the phenyl moieties or by substituting alternative fluorinated moieties. To the best of our knowledge, this is the first time these compounds have been identified as anion receptors. Battery cells have been fabricated and tested using several of these *as-prepared, unpurified* anion receptors, with specific discharge capacities on the order of 50-80 mAh/g at discharge voltages near 5V. Further improvements in specific capacity and Coulombic efficiency are expected by incorporating purification methods following anion receptor synthesis.

^{19}F NMR studies of solutions of these fluorophenyl boroxines in propylene carbonate with and without LiF strongly suggest that these compounds can bind fluoride at several non-equivalent boron sites with varying binding energies, as predicted by the modeling studies. ^{7}Li NMR indicates that the diffusion coefficient of Li in these solutions is comparable to other well-known anion receptors such as tris (pentaflurophenyl) borane. [11]B studies are underway to elucidate the nature of the boron-fluoride binding for these compounds in solution.

Ab initio modeling coupled with experimental studies suggest a trend in anion receptor binding energy and practical cathode specific capacity, which indicates weaker binding energies should provide more favorable cathode specific capacities. As such modeling and experimental work was re-focused on weaker rather than stronger binding compounds.

Recommended Follow-On Studies
Based on the progress to date in developing new anion receptors with tailor-able fluoride binding properties, a highly focused follow-on study is recommended. This study would help to identify optimal anion receptor designs that allow for facile fluoride capture and release energetics to facilitate reversible high specific energy cathodes for use in dual ion intercalating batteries. This follow-on study would consist of:
1) Ab initio calculations to identify targeted fluorophenyl and other substituted boroxine compounds with fluoride binding energies *between -65 and -20 kcal/mol* at Caltech under the direction of Prof. Bill Goddard and Dr. Mario Blanco.
2) Synthesis, *purification, and characterization* of these compounds in-house at JPL as well at the University of Missouri under the direction of Prof. Reddy Prakash.
3) Preparation and testing of dual ion intercalating test cells (in coin cell and 18650 formats) incorporating these *new highly purified anion receptors* at JPL under the direction of Dr. William West.

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Introduction

To meet the demand for high specific energy batteries for military, aerospace, and commercial applications, a novel dual ion intercalating lithium – fluoride battery was conceived. This new battery cell chemistry is based upon the dual intercalation of lithium and fluoride ions into graphite electrodes. These cells may have a factor of 3-5 greater specific energy over state-of-art Li-ion batteries, based on:

- Higher cell voltage: >5 V versus <4V for state-of-art Li-ion cells
- Higher specific capacity: 680-2200 mAh/g cathode specific capacity versus state-of-art 140-180 mAh/g cathode specific capacity

Through a preliminary study, proof of concept of this novel lithium - fluoride dual ion intercalating battery system was demonstrated, validated by a number of experimental means.[1] These cells operate at upwards of 5V as predicted, but thus far have fallen well below specific capacity projections. In this previous study, a key variable in dictating cell performance was identified: the chemistry of an anion-binding electrolyte additive.

The purpose of this project was to carry out a hierarchical theoretical (quantum mechanical) study coupled with an experimental battery cell study of anion binding compounds in order to target optimal binding energetics to allow for facile anion capture and release kinetics, and thus greatly improved battery cell specific energy. After identification of promising anion binding agents, the goal was to either procure or synthesize these compounds, and then prepare a series of electrolyte formulations using the anion receptors and preferred solvents and salts. The compounds were to be tested by a number of electrochemical means, including cell level studies to allow for the determination of the degree of fluoride (de)intercalation, the associated electrode and electrolyte kinetics, and the practical electrode and cell-level specific energy.

The modeling and experimental work was to tie closely together in a feedback loop, with experimental data providing refinements to the model for improved screening of promising molecular designs. This combination of theory and experiment may prove to be much more cost effective than a large experimental screening effort and lead to a more fundamental methodology for future improvements of cell design and performance, potentially bringing to fruition this highly attractive and novel battery chemistry.

Experimental Results

Anion Receptor: boron tris(trifluoroacetate)

In a concurrently funded Army CECOM project, the compound boron tris(trifluoroacetate) was identified as a promising anion receptor candidate. Attempts at synthesis by a commercial vendor were unsuccessful. However, Professor V. Reddy Prakash of the University of Missouri agreed to prepare the pure compound (Fig. 1) at no charge.

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[1] "Reversible Intercalation of Fluoride-Anion Receptor Complexes in Graphite", William C. West, Jay F. Whitacre, Nicole Leifer, Steve Greenbaum, Marshall Smart, Ratnakumar Bugga, Mario Blanco, and S. R. Narayanan, *J. Electrochem. Soc.*, **154,** A929 (2007).
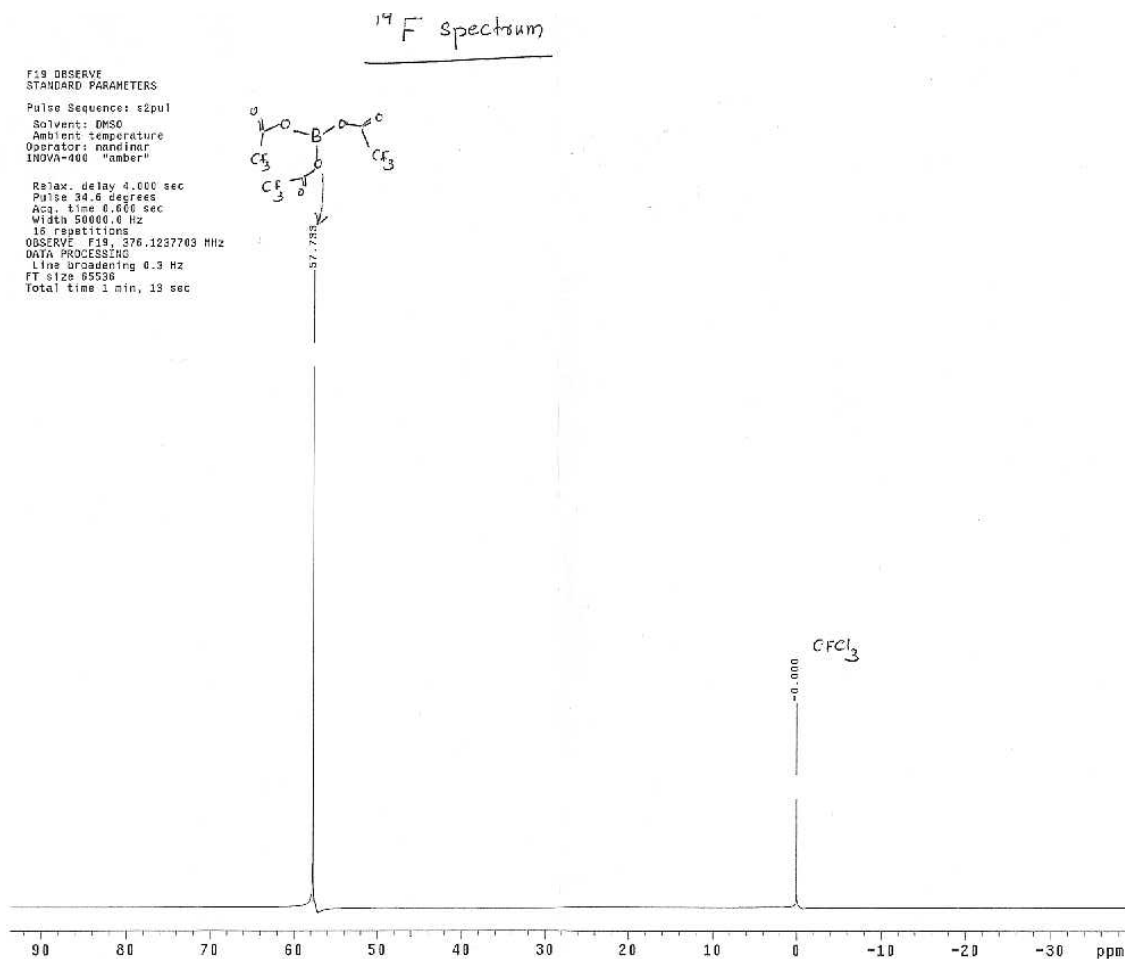
Fig. 1. ^{19}F-NMR spectrum of boron tris(trifluoroacetate).

Cell level studies of this new receptor incorporated both the conventional solvent, propylene carbonate, and new high anodic stability solvents including 2-fluorophenyl methyl sulfone and 4--fluorophenyl methyl sulfone (Fig. 2.).
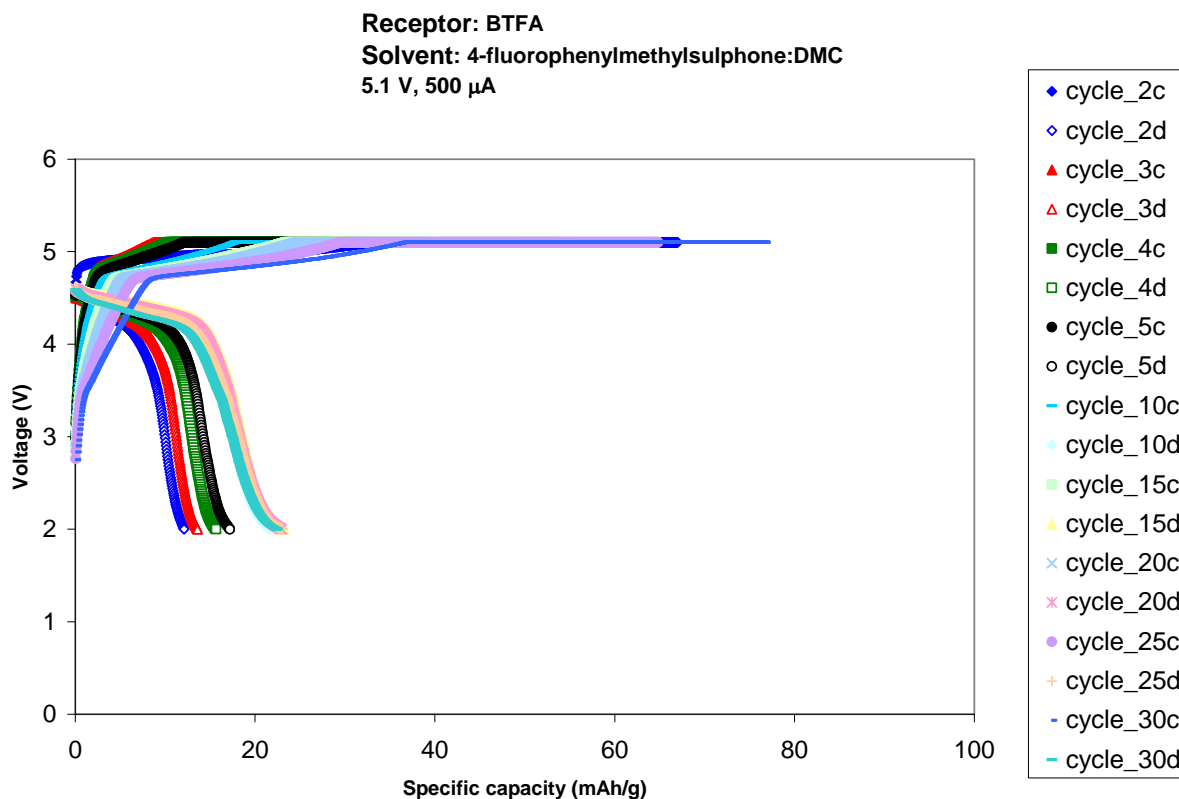
Fig. 2. Representative cathode specific capacity vs. voltage for boron tris(trifluoroacetate) anion receptor.

Unfortunately, the cathode specific capacity of the cells incorporating this new anion receptor was low compared with other anion receptors. It is noteworthy that the binding energy of this receptor to fluoride in the solvent was predicted to be -104 Kcal/mol, much higher than the baseline anion receptor tris hexafluoroisopropyl borate (THFIPB) at -72 Kcal/mol.

As a comparison, cells were fabricated using BF_3 (in the form of the lithiated salt $LiBF_4$) anion receptor. These cells showed comparable specific capacity to the tris pentafluorophenyl borane (TPFPB) (Fig. 3.). Note that the binding energy of the BF_3 anion receptor to the fluoride in solvent is predicted to be -82.7 Kcal/mol, nearly the same as for TPFPB of -79 Kcal/mol.
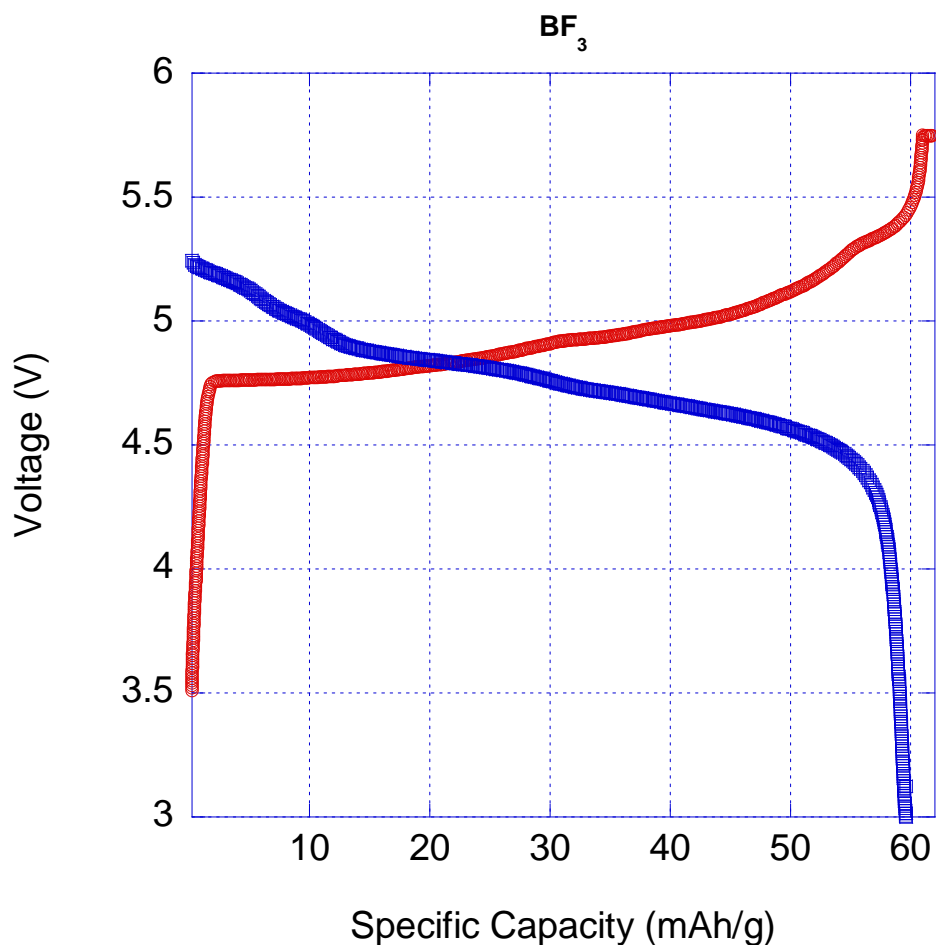
Fig. 3. Representative cathode specific capacity vs. voltage for BF_3 anion receptor (in the lithiated salt form $LiBF_4$).

From these data, and from previous and/or concurrent studies of other anion receptors, it is instructive to compare the predicted binding energy of the anion receptors to the practical specific capacity (Fig. 4.).
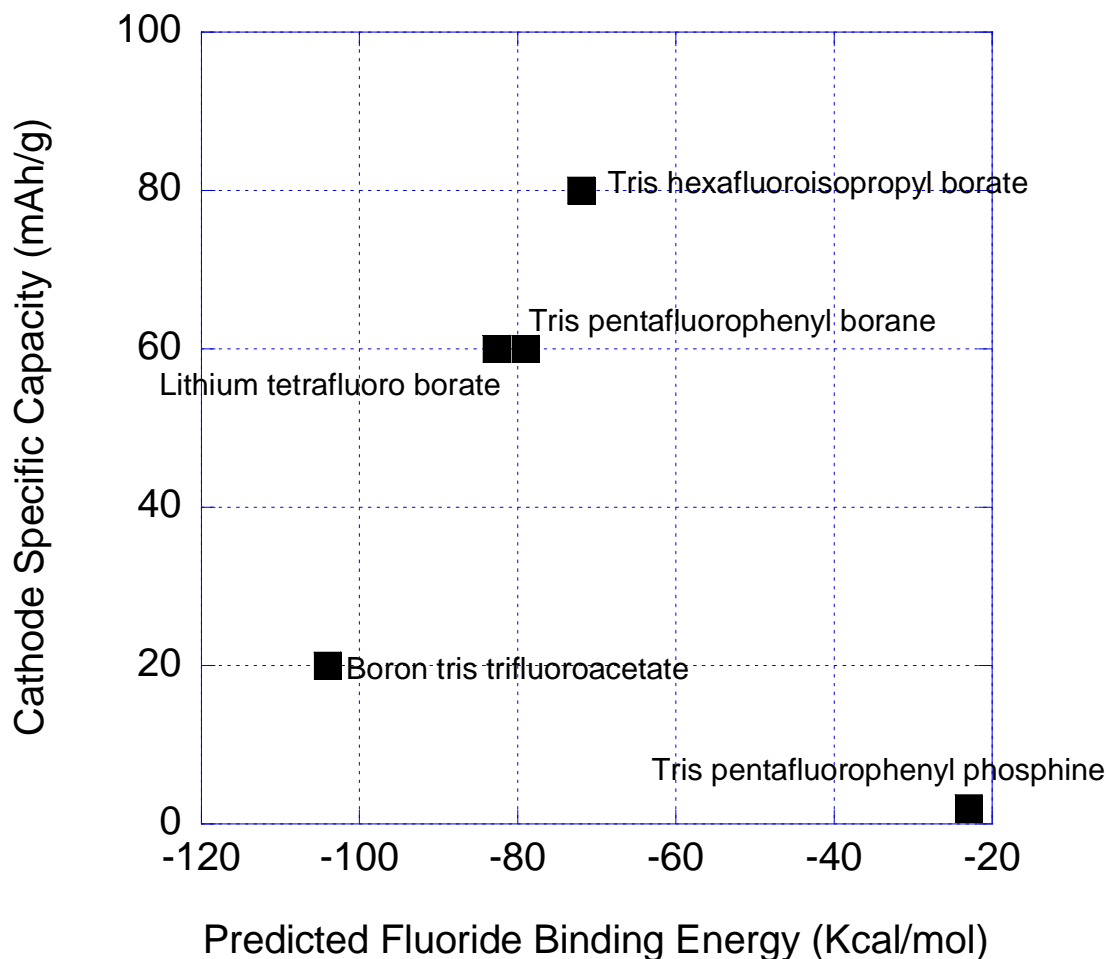
Fig. 4. Cathode specific capacity as a function of predicted fluoride binding energies for various anion receptors.

Fig. 4 is an oversimplification in that it does not reflect key attributes regarding the anion receptor anodic or cathode stability, solubility, and so on (which of course can dictate the anion receptor performance). Nonetheless, it appears that the cathode specific capacity passes through a maximum (of unknown magnitude) at moderate fluoride binding energy. As such, further work will focus on both validating this trend, as well as identifying other anion receptors that have binding energies between -20 and -70 Kcal/mol.

Anion Receptor Type: Fluorophenyl boroxines
Most boronic acids readily undergo dehydration (Fig. 5.) to form the cyclic trimeric anhydrides (e.g. boroxine; 1,3,5,2,4,6-trioxatriborinane). This often tends to occur spontaneously at room temperature, or in the course of drying.[2]

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[2] Boronic Acids: Properties and Applications, Alfa Aesar product manual:
http://www.alfa.com/media/pdf/brochures/Boronic%20Acid%20Brochure.pdf (2008).
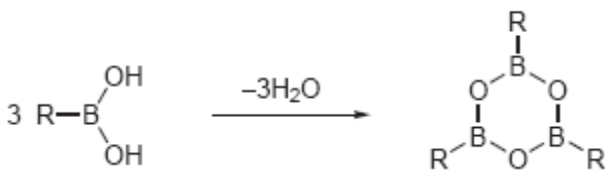
Fig. 5. Dehydration of boronic acid to form cyclic boroxines.[1]

Given the relative ease in preparation, low cost of the precursors, and wide range of possible structural combinations, this class of compounds was examined as a candidate class of anion receptors. Several variants were prepared by first dissolving the fluorophenyl boronic acids (e.g. difluorobenzene boronic acid, trifluorobenzene boronic acid, pentafluorobenzene boronic acid) in a solvent such as water or acetone, and then dehydrating. The resultant boronic acid anhydrides were dissolved in propylene carbonate to probe the solubility for use as anion receptors in dual ion intercalating battery cells. The solubility was found to be (qualitatively) strongly dependent on the degree and type of fluorination (Fig. 6). It is expected that by decreasing the symmetry of the boroxines (by preparing with varying fluorophenyl moieties), the solubility can be further improved.

Fig. 6. 0.06M fluorinated boroxines in propylene carbonate. From left: 1, 3, 5 *tris* (difluorophenyl) boroxine, 1, 3, 5 *tris* (trifluorophenyl) boroxine, 1, 3, 5 *tris* (pentafluorophenyl) boroxine.

Battery test cells were fabricated and tested using these new anion receptors. It was found that several of these boronic acid anhydrides functioned quite well as anion receptors in the dual ion intercalating cells. The specific discharge capacity of the cells generally increased with cycling, to roughly 50-60 mAh/g (Fig. 7). The Coulombic efficiency of these cells was poor-approximately 50%. However, given that the anion receptors were used as-prepared, with no purification steps, it is not surprising that the Coulombic efficiency was low. Purification steps are now being explored to decrease the contamination levels which very likely will increase the specific discharge capacity, cycle life, and Coulombic efficiency.
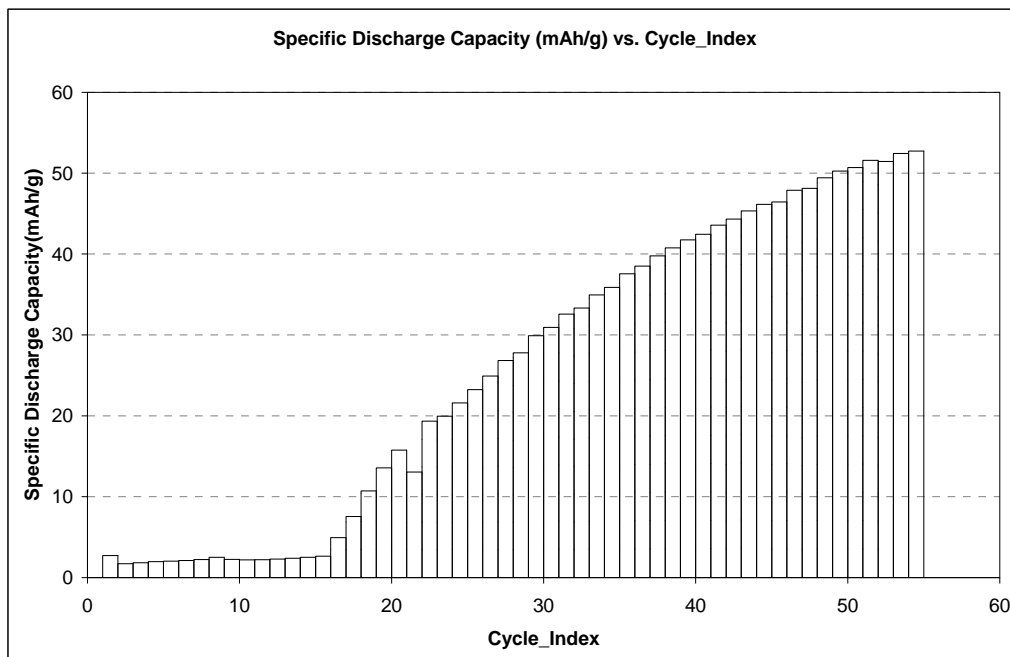

Fig. 7. Representative cathode specific capacity vs. cycle number for graphite cathode|diflurophenyl boroxine)+PC+LiF|Li anode cells.
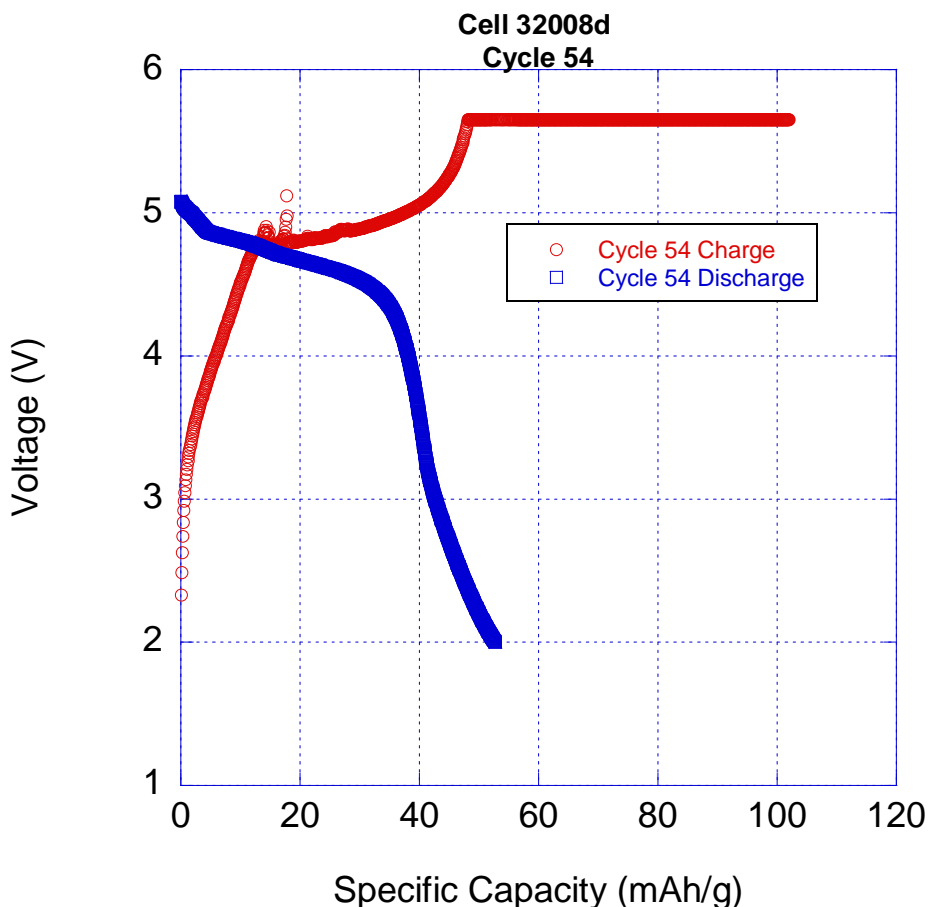
Fig. 8. Representative cathode specific capacity vs. voltage for graphite cathode|diflurophenyl boroxine)+PC+LiF|Li anode cells.

NMR Studies of fluorophenyl boroxines

In order to understand the fluoride binding characteristics of these new anion receptors, an NMR study was carried out. The materials were prepared as follows:

1) Prepare the fluorinated boroxines:
   a. Dissolve 1 gram difluorobenzene boronic acid in 5 ml methanol. Dry on a 100°C hot plate for 1 hour in the dryroom. Grind powder and put it in a labeled vial as "DF".
   b. Dissolve 1 gram trifluorobenzene boronic acid in 5 ml methanol. Dry on a 100°C hot plate for 1 hour in the dryroom. Grind powder and put it in a labeled vial as "TF".
   c. Dissolve 1 gram pentafluorobenzene boronic acid in 5 ml methanol. Dry on a 100°C hot plate for 1 hour in the dryroom. Grind powder and put it in a labeled vial as "PF".
   d. Dissolve 0.373g difluorobenzene boronic acid + 0.415g trifluorobenzene boronic acid + 0.50g pentafluorobenzene boronic acid in 5 ml methanol. Dry on a 100°C

hot plate for 1 hour in the dryroom. Grind powder and put it in a labeled vial as "DF-TF-PF".

2) Prepare the following solutions from the dried compounds listed above, and seal them in labeled vials:
   a. Solvent + LiF:
      i. 2ml of 0.2M LiF in PC (= 0.010g LiF in 2 ml PC)
   b. Solvent + receptor:
      i. 2ml of 0.1M DF (=0.084g) in PC
      ii. 2ml of 0.1M TF (=0.095g) in PC
      iii. 2ml of 0.1M PF (=0.116g) in PC
      iv. 2ml of 0.1M DF-TF-PF (=0.098g) in PC
      v. 2ml of 0.1M TPFPB (=0.102g) in PC

   c. Solvent + receptor + LiF:
      i. 2ml of 0.2M LiF in PC (= 0.010g LiF in 2 ml PC) + 0.1M DF (=0.084g)
      ii. 2ml of 0.2M LiF in PC (= 0.010g LiF in 2 ml PC) + 0.1M TF (=0.095g)
      iii. 2ml of 0.2M LiF in PC (= 0.010g LiF in 2 ml PC) + 0.1M PF (=0.116g)
      iv. 2ml of 0.2M LiF in PC (= 0.010g LiF in 2 ml PC) + 0.1M DF-TF-PF (=0.098g)
      v. 2ml of 0.2M LiF in PC (= 0.010g LiF in 2 ml PC) + 0.1M TPFPB (=0.102g)

PC=propylene carbonate (solvent),   LiF=lithium fluoride (salt)
DF=difluorophenyl boroxine (receptor),
TF= trifluorophenyl boroxine (receptor)
PF=pentafluorophenyl boroxine (receptor)
DF-TF-PF=solid solution of above receptors, TPFPB=tris pentafluorophenyl borane (known receptor)

Initial observations indicated that all of the receptor –only mixtures are solutions except for 2 - the 0.1 M PF and DF in PC. In these two mixtures, white powder settled on the bottom of the sample. All of the receptor-LiF mixtures and the LiF only are solutions.

Fluorine-19 data are presented below. The reference used was lithium triflate. The probe has a F background, and thus echo sequences were used to suppress it. For a given receptor each chart shows two curves: one for the sample with LiF and one for the sample without LiF. For all of the systems, there was at least one common peak in the curves. For all of the receptor except DF there is at least one additional peak visible upon addition of the LiF. DF has an additional peak in the LiF-free sample. The intensities of the LiF-free sample with DF were very low and had to be multiplied by 25 in order to be the same order of magnitude as the sample with LiF. There is a difference in the intensities of the common peaks at a given location. In the LiF only sample, there was no F signal observed (only background is visible), indicating there was no F present. This is an important conformation that PC cannot dissolve LiF without the aid of an anion receptor.
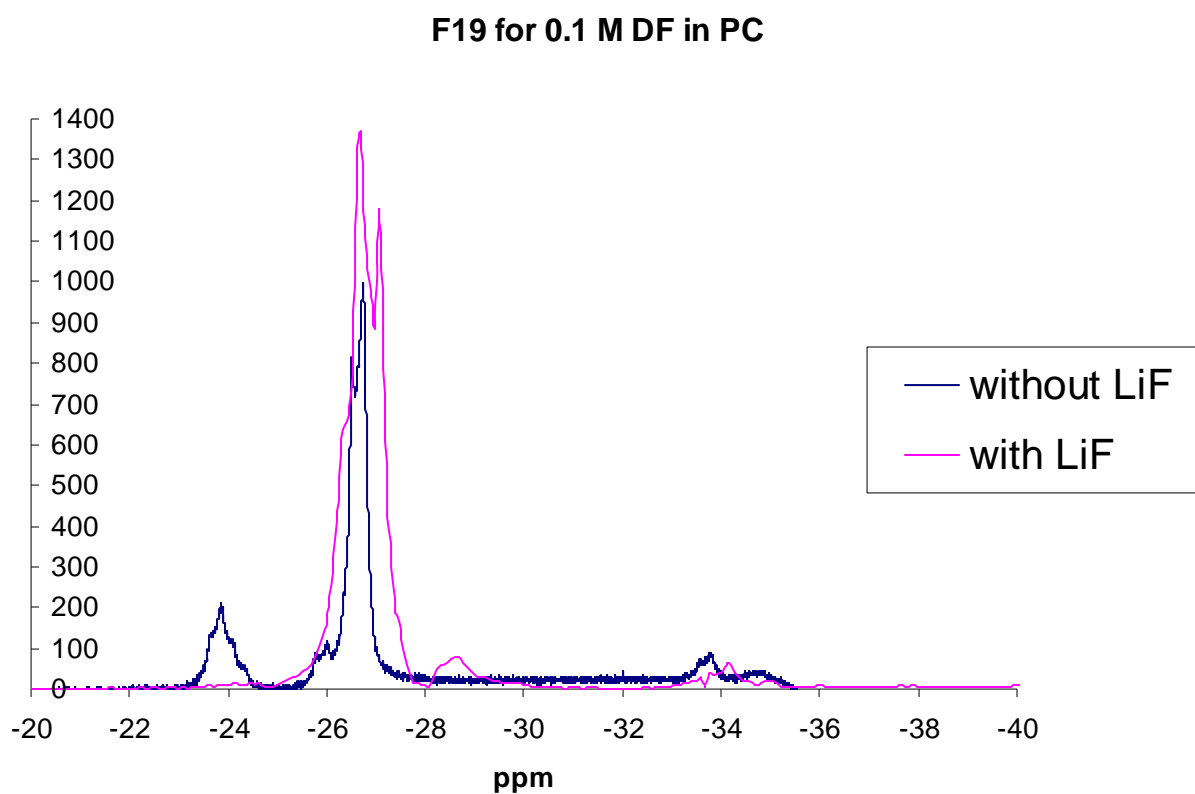
Fig. 9. ^{19}F NMR data of 0.1M difluorophenyl boroxine in propylene carbonate, with and without LiF.

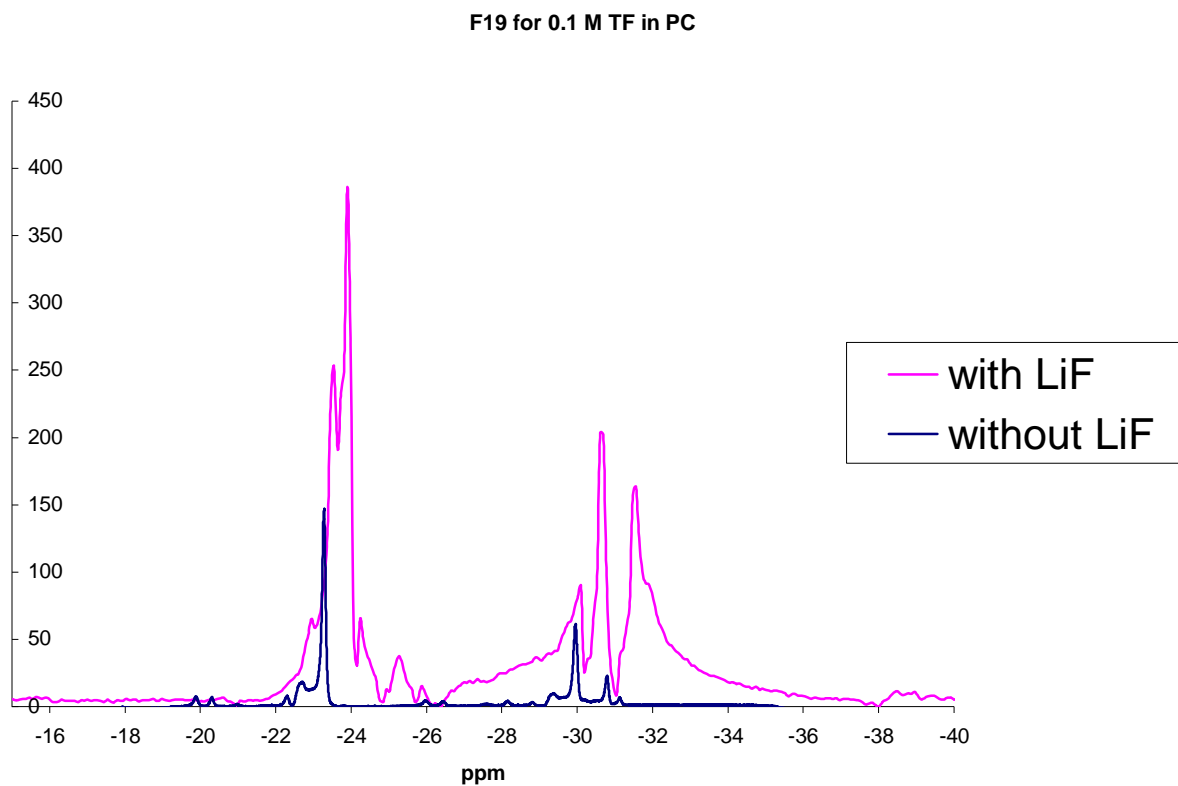**Fig. 10.** ^{19}F NMR data of 0.1M trifluorophenyl boroxine in propylene carbonate, with and without LiF.

F19 for 0.1 M PF in PC

Fig. 11. ^{19}F NMR data of 0.1M pentafluorophenyl boroxine in propylene carbonate, with and without LiF.

F19 for 0.1 M DF-TF-PF in PC

Fig. 12. ^{19}F NMR data of 0.1M difluorophenyl-trifluorophenyl-pentafluorophenyl boroxine in propylene carbonate, with and without LiF.

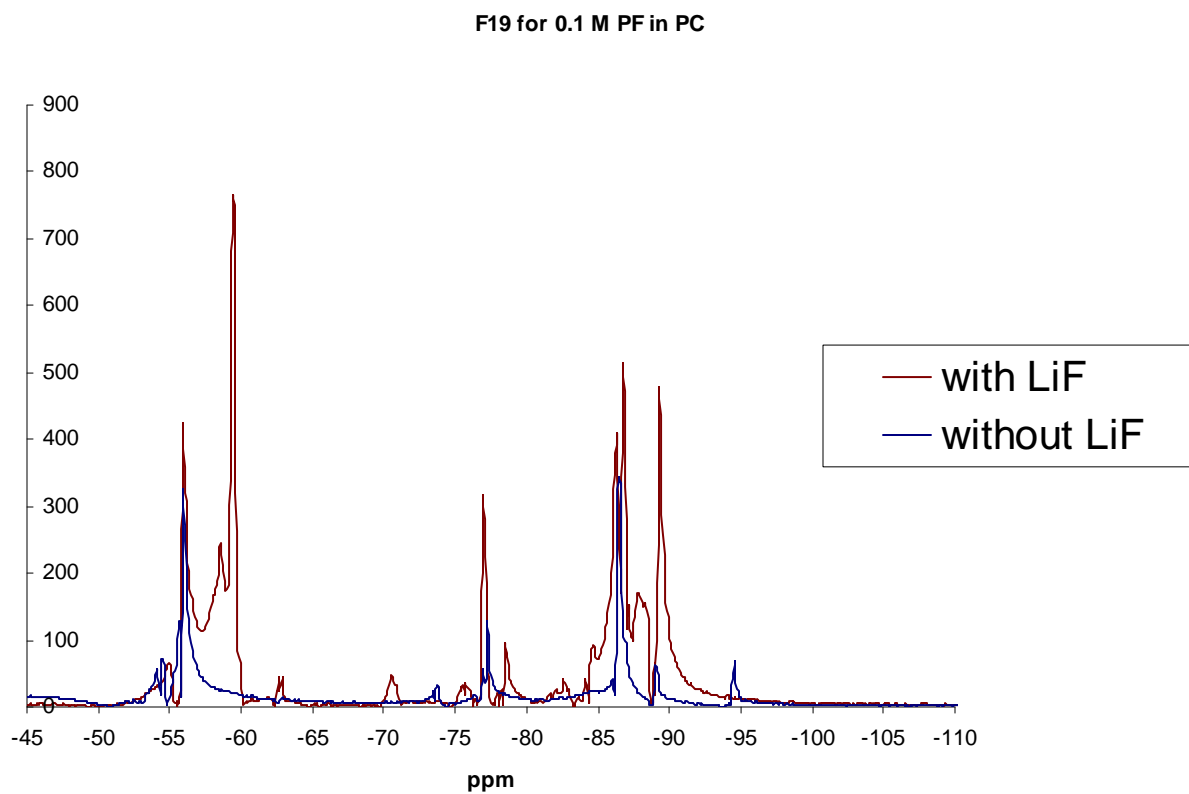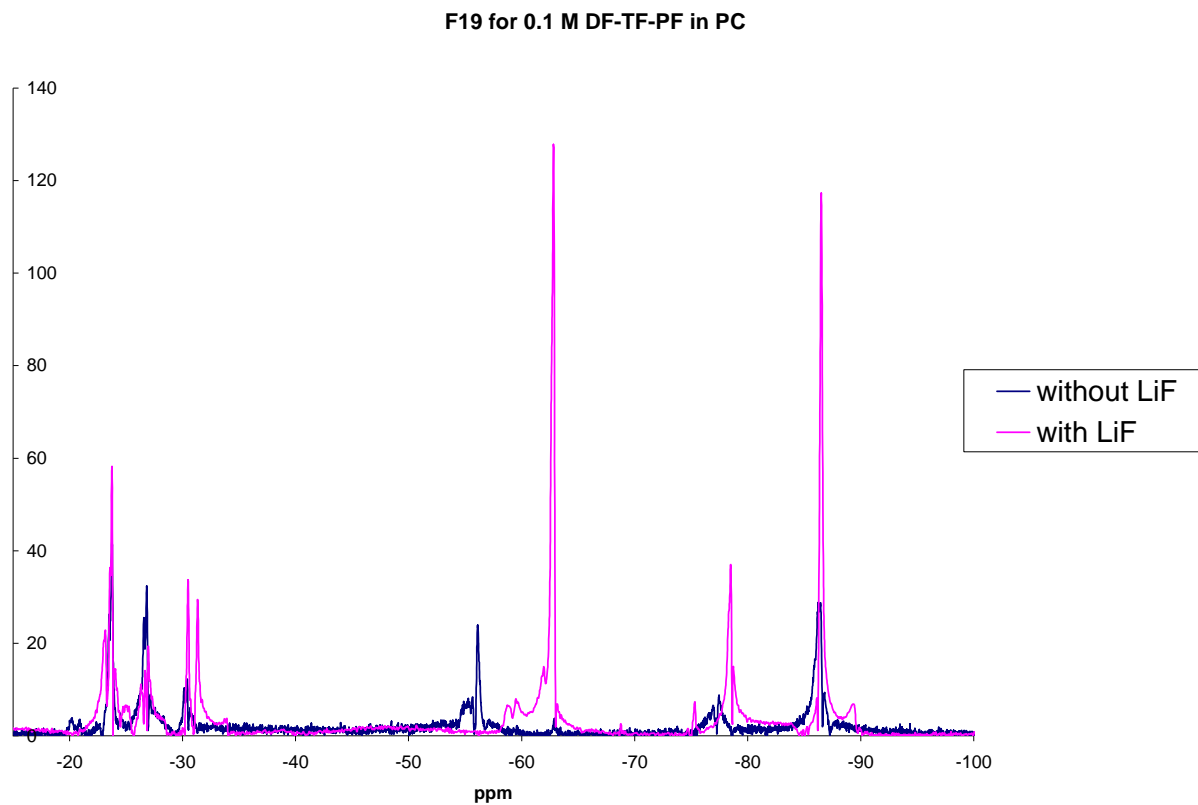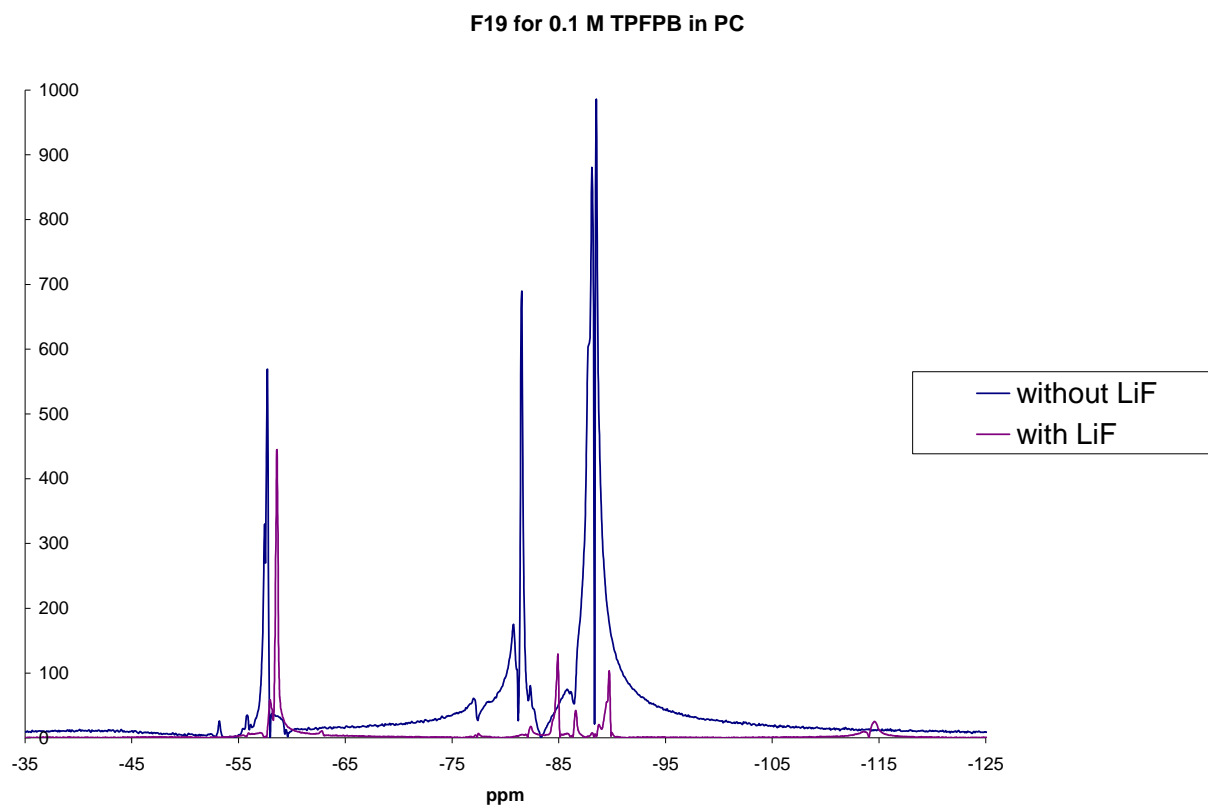**Fig. 13.** ^{19}F NMR data of 0.1M tris (pentafluorophenyl) borane in propylene carbonate, with and without LiF.
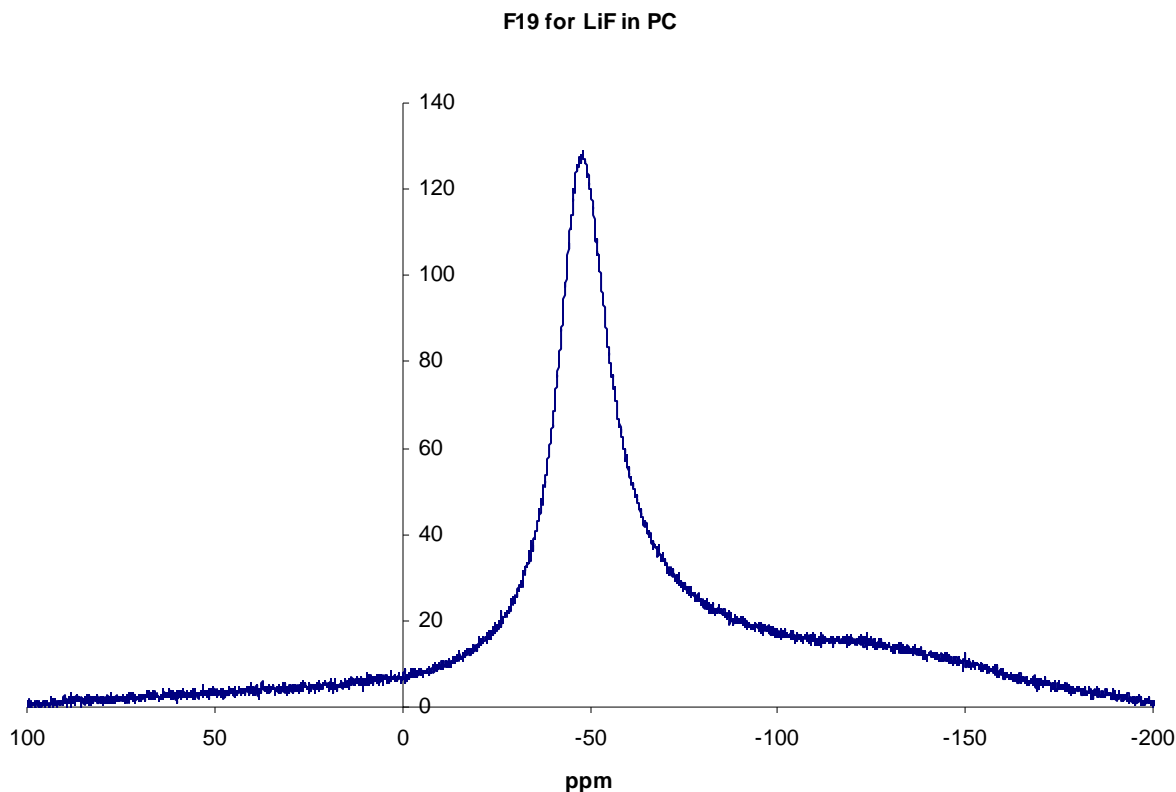
F19 for LiF in PC

Fig. 14. ^{19}F NMR data of LiF in propylene carbonate. Note that no appreciable fluoride is detected, confirming the necessity of anion receptors to yield LiF dissolution in the solvent.

^{7}Li data is presented below for the samples containing LiF. The reference used was LiCl. These data differ greatly depending on the receptor present. Two peaks can be seen in the spectra for LiF with DF, PF and TPFPB. The ratio of the intensities of these two peaks differs greatly for these three systems. In the TPFPB sample, the peak farthest upfield is split. Only one peak is seen in the other systems. All of the peaks in all of the spectra, except for TPFPB, have a chemical shift of approximately -1 ppm. For the multiple peak spectra (except TPFPB), both peaks are between 0 and -1 ppm. The peaks for TPFPB are located at approximately 0.5 and -0.5 ppm. The widths of the peaks also vary. In the DF and TF –containing systems, the widths are about 0.5 ppm. In the PF, DF-TF-PF-containing spectra, the widths are about 1 ppm. In the TPFPB-containing sample, the peaks widths are closer to 0.5 ppm than 1 ppm. There was no signal for the LiF only sample, indicating there was no LiF present. Given the fact that there was no LiF present in the sample containing no receptor, the differences between the spectra seem to indicate that the receptors allow for different levels of solubility of LiF in PC.

From these data, is it possible to estimate the diffusion constant of Li$^+$ in solution (Table I). The diffusion constant depends on the degree of fluorination on the phenyl moiety, and in all cases is on par with the well known anion receptor tris (pentafluorophenyl) borane.
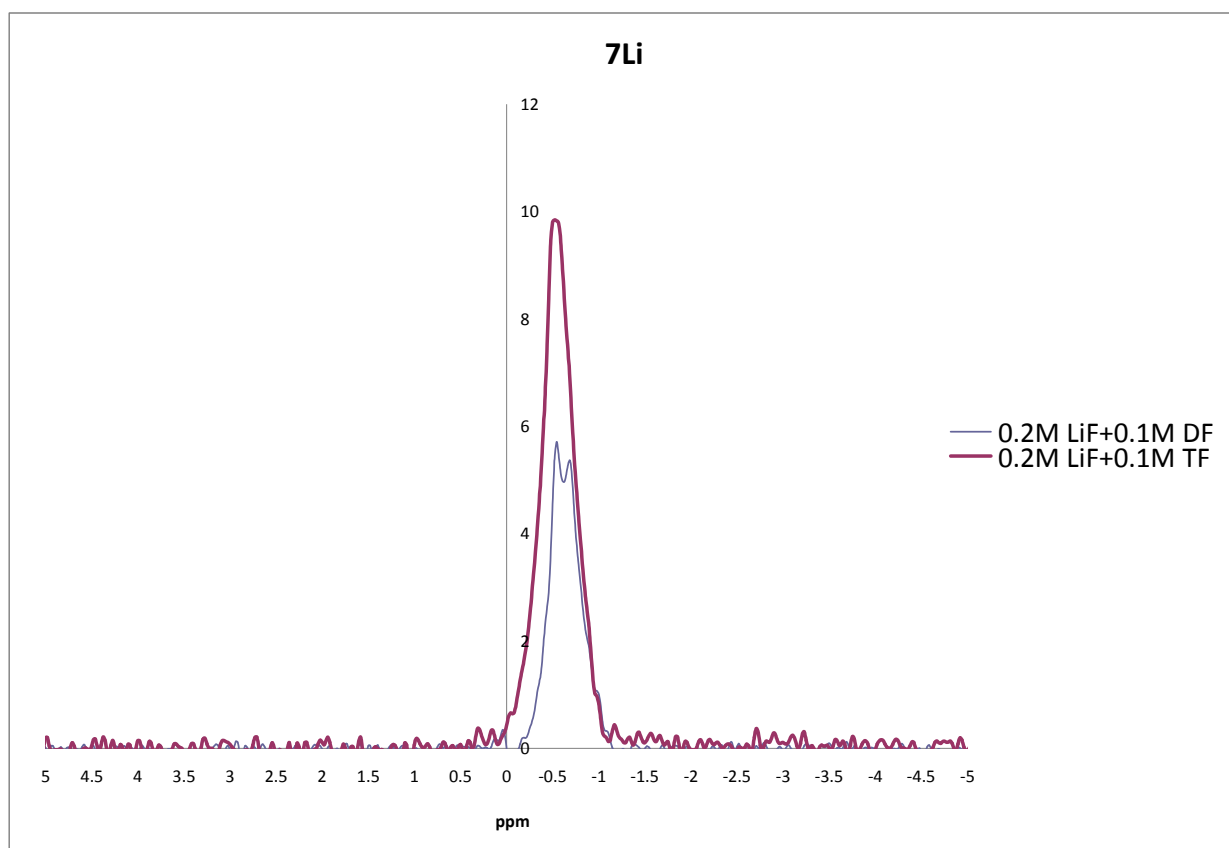
16

Fig. 15. ^{7}Li NMR data of LiF in various fluorophenyl boroxines in propylene carbonate.
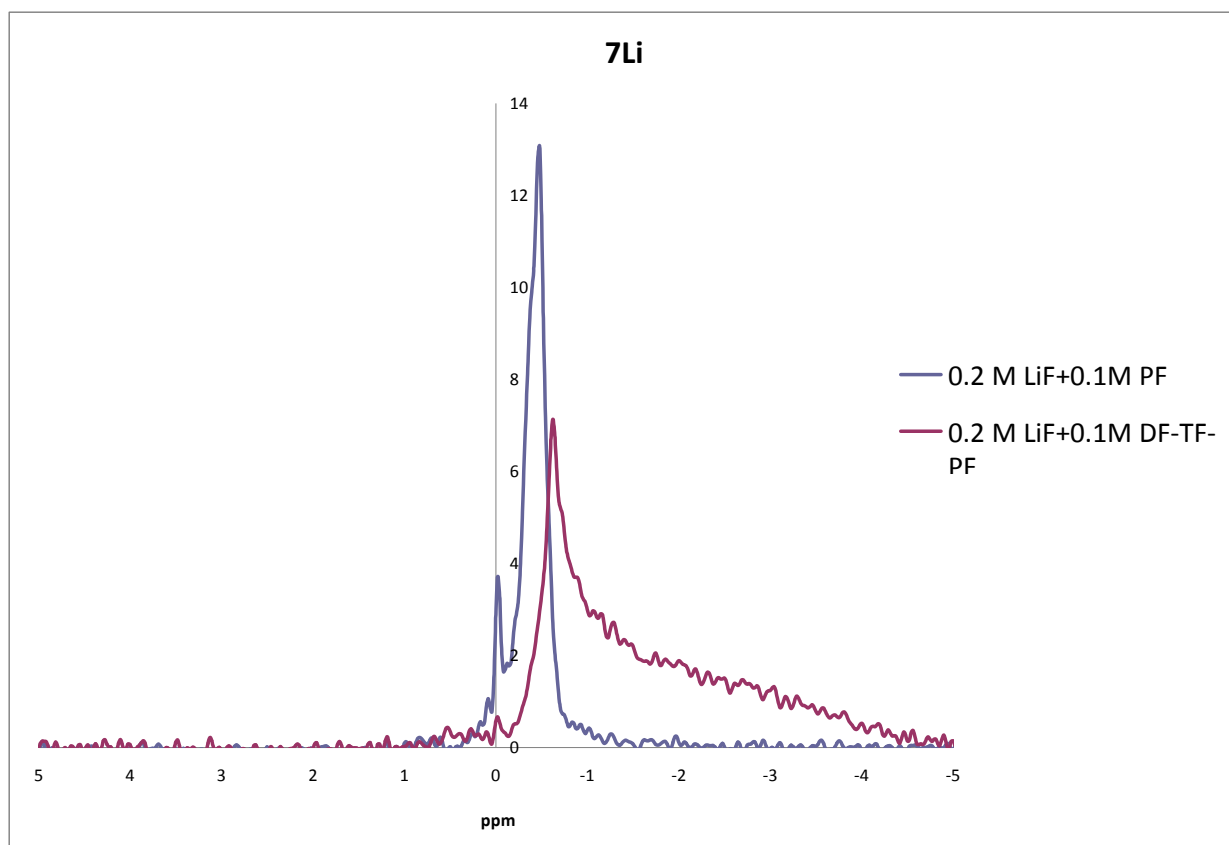
Fig. 16. ^{7}Li NMR data of LiF in various fluorophenyl boroxines in propylene carbonate.
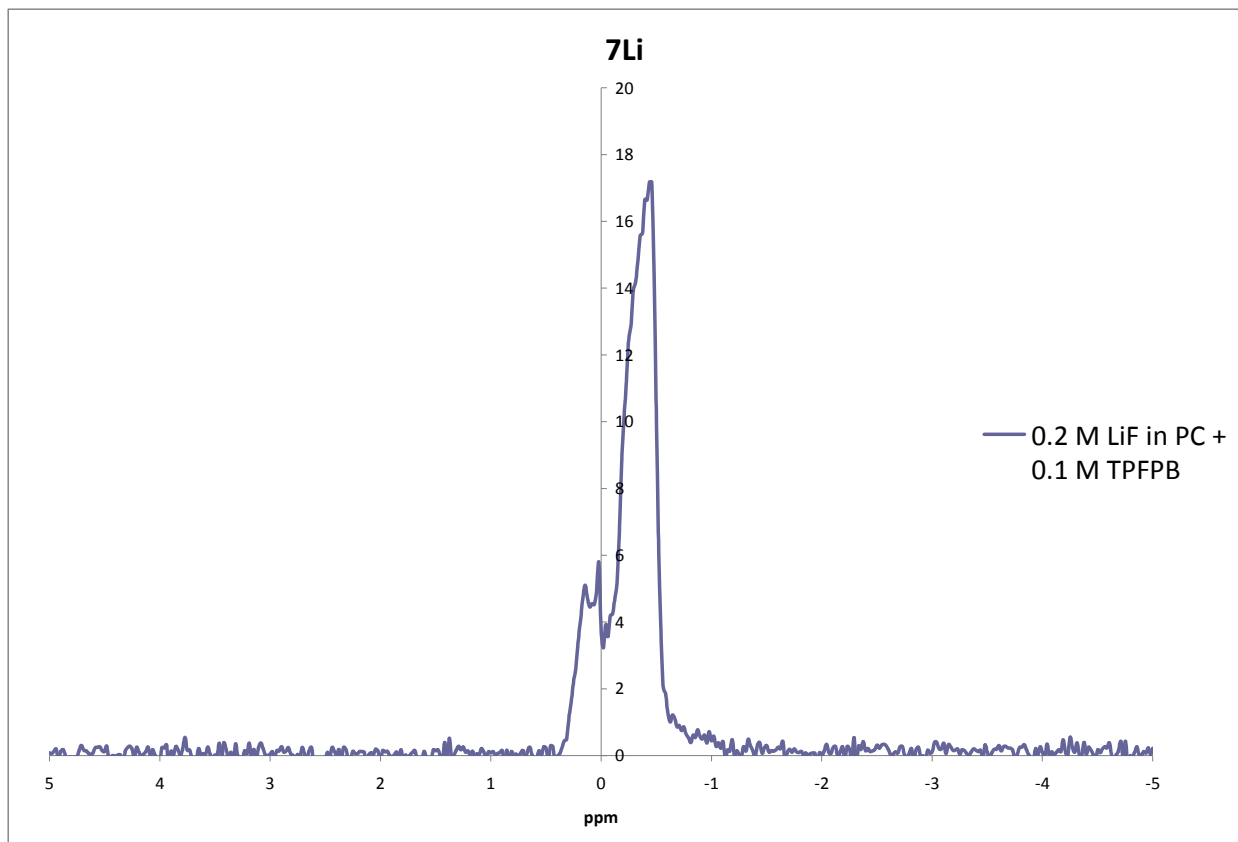
Fig. 17. ^{7}Li NMR data of LiF with various fluorophenyl boroxines in propylene carbonate.

Table I: Li$^+$ diffusion constants in various solutions by ^{7}Li NMR.

Compound	D lithium [*10^-6]
0.2M LiF + TPFPB in PC	2.12 (23.9C)
0.2M LiF + TF in PC	1.99 (23.6C)
0.2M LiF + PF in PC	1.96 (24.4C)
0.2M LiF + DF-PF-TF in PC	1.88 (24.1C)
0.2M LiF + DF in PC	1.98 (23.8C)

Modeling Results

We report on thermodynamics of the fluoride anion receptor 3,5 difluorbenzene boronic acid, DFBA, as well as the thermodynamic stability of the recently tested boron tris(trifluoroacetate), BTTFA, as a means to explained recent experimental observations.

1.   Modeling (QM/Density Functional Theory) of thermodynamics of Fluoride anion receptor binding: DFBA

We provide thermodynamic data calculated using Quantum Mechanical Density Functional Theory (B3LYP) for reactions of fluoride anion binding to two anion receptors:

3, 5 difluorobenzene boronic acid + **F-   -> 3**, 5 difluorobenzene boronic acid Fluoride-   **(1)**

and

perfluorinatedbenzene boronic acid + **F-   -> 3**, 5 perfluorinatedbenzene boronic acid Fluoride-   **(2)**
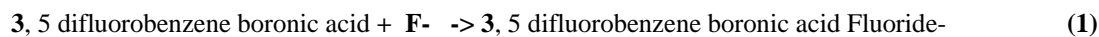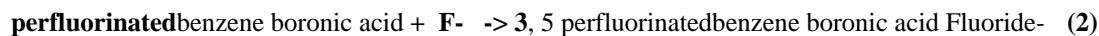
The individual electronic energies for each species are presented in Table II. The B3LYP functional was used and the geometries and final energies include solvation effects. These were optimized using a dielectric continuum model for propylene carbonate.

As a shorthand we refer to 3,5 difluorobenzene boronic acid as DFBA and the perfluorinatedbenzene boronic acid as PFBBA. We add an F to indicate the anion species (F-captured). The energy of the free fluoride anion in solution (propylene carbonate) is denoted F-carb. The binding energy is calculated as the difference of electronic energy between products and reactants, including solvation effects:

 E(reaction)   = E(AnionReceptorF-) - E(AnionReceptor) – E(F-)

Electronic energies are given in Hartrees while binding energies in Kcal/mol. All values are in solution. The conversion factor between Hartrees and Kcal/mol is

1 Hartree= 627.50955 Kcal/mol

The structures of these two anion receptor molecules are depicted in Fig. 18 and Fig. 19.

Table II: B3LYP DFT electronic energies for individual molecular components in Equation (1) and (2) fluoride anion receptors

DFBA LACVP** UDFT B3LYP
DFBA   -841.4153196
DFBAF   -941.4056588
F-carb-b3lyp-udft.out lacvp**   -99.90947179

Binding Energy   **-50.75**   Kcal/mol

PFBBA LACVP** UDFT B3LYP
PFBBA   -2329.86181
PFBBAF-b3lyp   -2429.891177
F-carb-b3lyp-udft.out lacvp**   -99.90947179

Binding Energy   **-75.24**   Kcal/mol
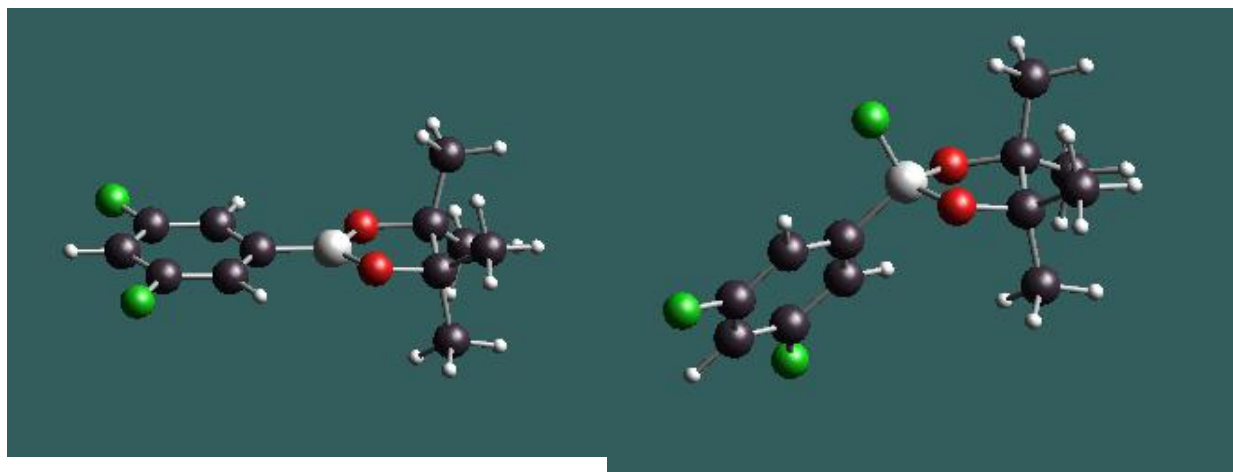
(a)   **(b)**

Fig. 18. Structure of unbound (a) and (b) fluoride bound DFBA anion receptor.
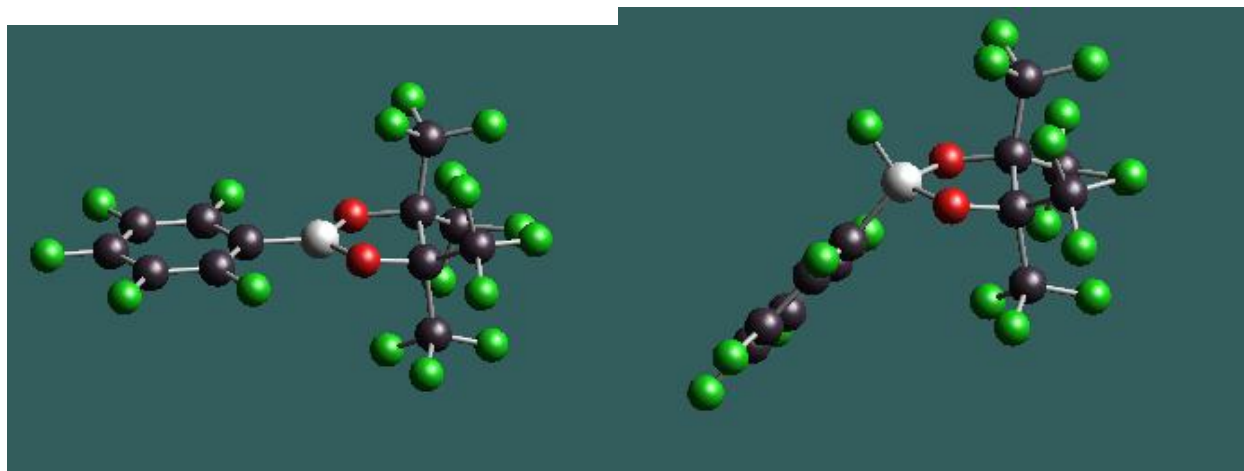
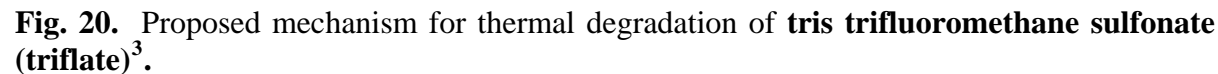**Fig. 19.** Structure of unbound (a) and (b) bound PFBBA

2. Potential dimerization of and electrochemical decomposition of BoronTris(trifluoroacetate) (BTTFA)

TTFBA was previously calculated to be a strong fluoride anion receptor (see table III below).

Table III.

Scheme	Class	Chemical Name	Study Name	B3LYP *Kcal/mol*	PWPW91 *Kcal/mol*	Solvation *Kcal/mol*
1	A	*tris (pentafluorophenyl) borane*	TPFB	**-79**	**-86**	**-4.5**
2	A	*tris (hexafluoroisopropyl) borate*	THFIPB	**-72**	**-81**	**-6.5**
3	A	*boron tris (trifluoroacetate) (CF3COO)3B*	BTTFA	**-104**	**-107**	**-7.3**
4	A	*2,6,7-Trioxa-1-borabicyclo[2.2.2]octane*	TRIOXAH	**-95**	**-102**	**-11.2**
5	A	*boric oxide*	B2O3	**-95**	**-101**	**-10.2**
6	B	*2,6,7-Trioxa-1-borabicyclo[2.2.2]perfluoro-octane*	TRIOXA	**-140**	**-119**	**-3.5**
7	D	*2.8,9-Trioxa-1-phosphabicyclo[3.3.3]undecane*	P-BICYCLO	**-28**	**-37**	**-6.4**
8	D	*tris (pentafluorophenyl) phosphine*	TPFP	**-23**	**-30**	**-2.7**

However, preliminary tests did not give a significant improvement over traditionally anion acceptors such TPFB or THFIPB, which are predicted to have lower binding energetics than BTTFA. Furthermore, improved performance was observed when the cell was cycled for multiple periods, although a limiting capacity was eventually reached, below a good figure of merit. Potential causes for the limiting capacity include: 1) Too high anion binding energy which precludes F- to be donated to the electrode, or 2) decomposition reactions of the anion-bound receptor. These potential causes are further discussed below.

Fig. 20. Proposed mechanism for thermal degradation of **tris trifluoromethane sulfonate (triflate)**[3]**.**

1) Binding energetics on the order of 70 Kcal/mol appear sufficient to achieve fluoride binding in electrochemical cells, such as in TPFB and THFIPB. Additional binding energy might simply add to the barrier needed for release of the anion at the intercalating graphite electrode during a charge cycle.

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[3] Olah, G. A.; Weber, T.; Farooq, O., The Thermal Cleavage of Boron Tris-Trifluoromethane-Sulfonate(Triflate) and Boron Tris-Pentafluoroethane-Sulfonate(Pentflate) to Triflic(Pentflic)Anhydride and Trifluoromethyl Triflate(Pentafluoroethyl Pentflate). *Journal of Fluorine Chemistry* **1989,** 43, (2), 235-241.

2) BTTFA suffers some chemical change during transit, or during cell operation which limits its potential as an anion acceptor.

Binding Energetics Too High:

Explanation (1) was discussed in our recent publication and it should be further considered once additional receptors with similar binding energetics are tested and their performance evaluated. Here we focus on the possibility of electrochemical changes, degradation and/or dimerization, of BTTFA.

In order to test this explanation further we are currently attempting the synthesis of an anion receptor, TRIOXA, predicted to have the highest binding energy encountered so far. The chemical structure of this anion receptor is shown below:
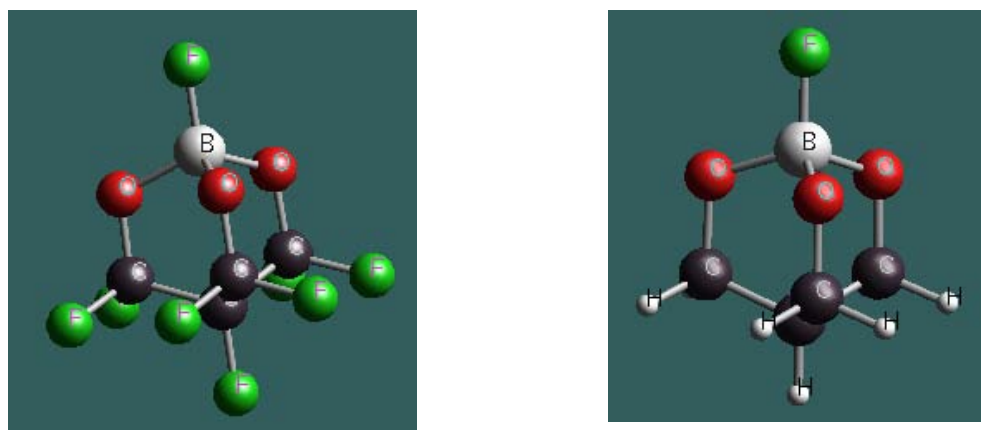
(a)   **(b)**

Fig. 21. (a) TRIOXA, a perfluorinated anion receptor shown in its anion form, with high binding energy. (b) Hydrogenated form of the receptor, TRIOXAH.

The binding energy 139.76 Kcal/mol, was computed, as usual, from the energies of individual molecular components

TRIOXA B3LYP lacvp** udft
trioxabicycloF-fine.out in PC   -1202.0015 C3v
trioxabicyclo-fine.out in PC   -1101.8693 C3v
F-carb-b3lyp-udft.out lacvp**   -99.9095

Binding Energy   **-139.76** Kcal/mol

The perfluorinated compound presents a difficult and expensive synthesis. Instead we opted for the synthesis of the hydrogenated analogue compound, TRIOXAH. The energetics are also

higher than traditional anion receptors, 94.52 Kcal/mol, but the lack of perfluorination makes it an easier target for synthesis.

TRIOXAH B3LYP lacvp udft**

trioxabicycloHF.out in PC	-507.2929087 C3v
trioxabicycloH.out in PC	-407.232812 C3v
F-carb-b3lyp-udft.out lacvp**	-99.90947179

Binding Energy   **-94.52 Kcal/mol**

One potential path towards anion receptors with higher capacity may be a reduction of binding energetics to values comparable to THFIPB and TPFPB. A uniform strategy has been found to accomplish this. It has been found by computation that a simple replacement of chemical groups bound to the boron center for fluorine atoms leads to lower binding energies in a controlled manner. For example, if we replaced one or two of the perfluorinated acetate groups in BTTFA we obtained the following predictions:

1 Trifluroacetate transmuted into an F atom

DTFBA B3LYP lacvp**

DTFBA.out:	-1177.201801
DTFBAF.out:	-1277.2683
F-carb-b3lyp-udft.out lacvp**	-99.90947179

Binding Energy   **-98.54** Kcal/mol

2 Trifluroacetate transmuted into two F atoms

TFBA B3LYP lacvp**

|	
TFBA.out:	-750.8789305
TFBAF.out:	-850.9341792
F-carb-b3lyp-udft.out lacvp**	-99.90947179

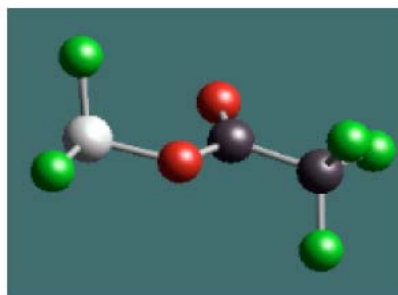Binding Energy   **-91.48** Kcal/mol

The corresponding chemical structures are shown in Fig. 22. The formation of these compounds, from BTTFA itself, is somewhat endothermic (around 35 Kcal/mol), see table below), but quite plausible. The reaction leads to a formation of a negative trifluoroacetate ion (TFA-) as a byproduct.
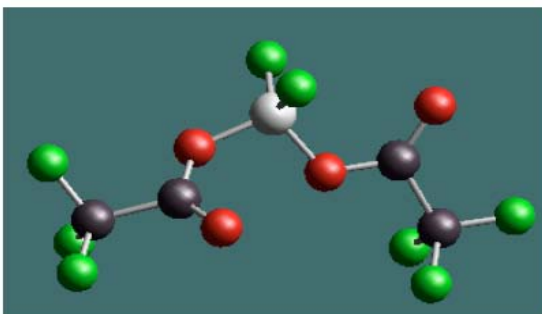
<div align="center">(a)   (b)</div>

Fig. 22. Analogues of BTTFA with F atom replacement of trifluoroacetate. (a) DTFBA, ditrifluoroboroacetate. (b) TFBA, Boron trifluoroacetate.

**Thermal Degradation Processes:**

Thermal degradation of a related compound, boron tris trifluoromethane sulfonate (triflate), was studied in 1988 in Prof. Olah's laboratory.[3] Decomposition occurred at 200 C, yielding boron trifluoride, sulfur dioxide, trifluoroacetyl fluoride, triflic(pentflic) anhydride, triflic(pentflic) triflate (pentflate) and boric acid. The mechanism shown in Fig. 20 was proposed by Olah's group.

If we replace B = B(OCOCF2CF3)3 and the sulfonate group, OSO2, with the carboxylate group, COO, the relevant decomposition compounds for BTTFA, under similar conditions, might include:

BF3, CF3COF, CF3CF2COO-OOCCF2CF3, CF3CF2COOCF2CF3, B2O3

Thermal Decomposition Reaction:

We have investigated the energetics of the analogous decomposition reaction:

B(CF3CF2COO)3 + B(CF3CF2COO)3   -> B2O3 + 3CO + 3 (CF3CF2COOCF2CF3)
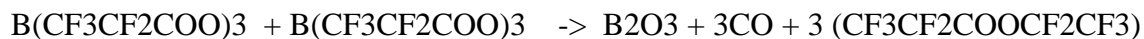
Dimerization/Decomposition Reaction:

Another potential reaction that may limit energy capacity is the dimerization-partial degradation reaction of the anion receptor:

<div align="center">26</div>

B(CF3CF2COO)3 + B(CF3CF2COO)3 ->   B2(CF3CF2COO)4 + CF3CF2COOCF2CF3 + CO2
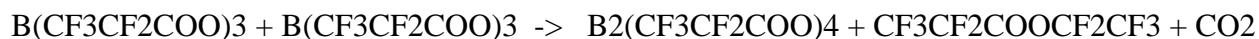
The energetics of all these reactions is shown below.

Intermediates	Energy (Hartrees)
DTFBA-F	-1277.2683
DTFBA	-1177.2018
TFAME	-863.8040
CO	-113.3069
B2O3	-275.5496
TFA-	-526.3341
BTTFA-F-C3	-1703.5990
BTTFA-Cs	-1603.5233
TFBA	-750.8789
BTTFA-BTTFA-ring	-2154.6192

Reaction	Reaction Energy (Kcal/mol)	
(1) 1st F- Ion Exchange	**39.6**	BTTFA-F -> DTFBA + TFA-
(2) 2nd F- Ion Exchange	**34.7**	DTFBA-F -> TFBA + TFA-
(3) Olah's Decomposition	**103.2**	2 BTTFA -> 3 TFAME + 3 CO + B2O3
(4) Dimerization/decomposition	**-151.1**	2 BTTFA ->BTTFA-BTTFA-ring + 2TFA-

TFA- = trifluroacetate anion in solution, CO= carbon monoxide, B2O3 = boric oxide
TFAME= CF3CF2COOCF2CF3

The structure of the dimer in ring form, BTTFA-BTTFA-ring is shown in Fig. 23.
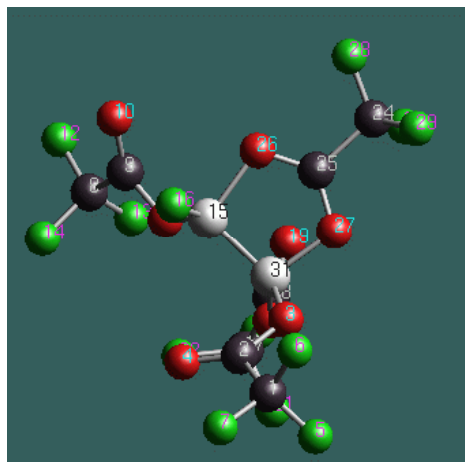

Fig. 23. Dimer of BTTFA. Stable form contains a five member ring.

Modeling Studies of Fluorophenyl Boroxines

Modeling studies were performed on the pure or mixed phenyl boronic anhydrides. Some representative compounds can be found on the last page of this report. For brevity we use the following notation:

DnPm ; DnTm ; DnPmFk n,m=0,1,2,3 k=1,2,3

D=difluoro phenyl
P=perfluorinated phenyl
M=monofluorinated phenyl
T=trifluorinated phenyl

So D2P1 means two difluorphenyl groups and one perfluorinated group while D2P1F represents D2P1 with a single captured F- anion, D2P1F2 two fluorines etc.

Method
We calculated thermodynamic data in the form of electronic energies and binding energetics using Quantum Mechanical Density Functional Theory (B3LYP) for reactions of fluoride anion binding to the boronic anhydride anion receptors. We use an open shell calculation (UDFT) with a good basis set (LACVP**) which translates to 6-31 G** basis set for main group elements.

Results
The anion receptor can capture a fluorine on a D,P,M, or T site. In all cases, except D2P1D, we computed F- capture by the highest degree of fluorination on the mixed anhydride phenyl group. Because these receptors could potential capture 1, 2, or even 3 (very unlikely due to repulsive electrostatics) fluorides since there are 3 boron in each compound. We computed the binding energetics for these multi-fluorinated compounds. The Fn designation indicates the number of captured fluorines in the anion receptor prior to the final capture.

Interestingly, the negative anion (A:F-) is still a good receptor (on the order of -40 Kcal/mol) to become A:(F-)2.

A simple analysis on the A:F- (single capture compounds) shows that binding energy depends quadratically on degree of fluorination, higher binding energies (more negative) correspond to higher degrees of fluorination on the phenyl groups. Once we have more data on the cathode specific capacities for these mixture boronic anhydrides we can use this expression to fine tune the degree of fluorination.

Table IV: Binding energetics of various fluorinated phenyl boronic acid anhydrides

Singly Charged Species

Compound	Degree of Fluorination	Binding Energy (Kcal/mol)
D0P3	15	-74.1
D1P2	12	-73.1
D2P1	9	-71.0

D2P1D	9	-70.0
T1P0	9	-69.3
D3P0	6	-67.5
M1P0	3	-61.6

Multi-charged (-2 and -3) species

D1P2F	13	-49.1
D2P1F	10	-45.9
D1P2F2	14	-16.6
D2P1F2	11	-11.2

Modeling Conclusions and further work:
In conclusion, all these anion receptor candidates are promising. Table I contains binding energetics for the dozen or so compounds investigated so far. It is important to note that any of the singly charged species with fluorination degrees ranging from 3 to 15 fall within the range of binding energies of interest for dual ion LiF intercalating batteries (between -45 to -80 Kcal/mol). Fig. 24 shows that the binding energy is a monotonic quadratic function of the degree of fluorination in these phenyl boronic anhydride compounds, providing the means for sequential and rational testing of their various electrochemistries.
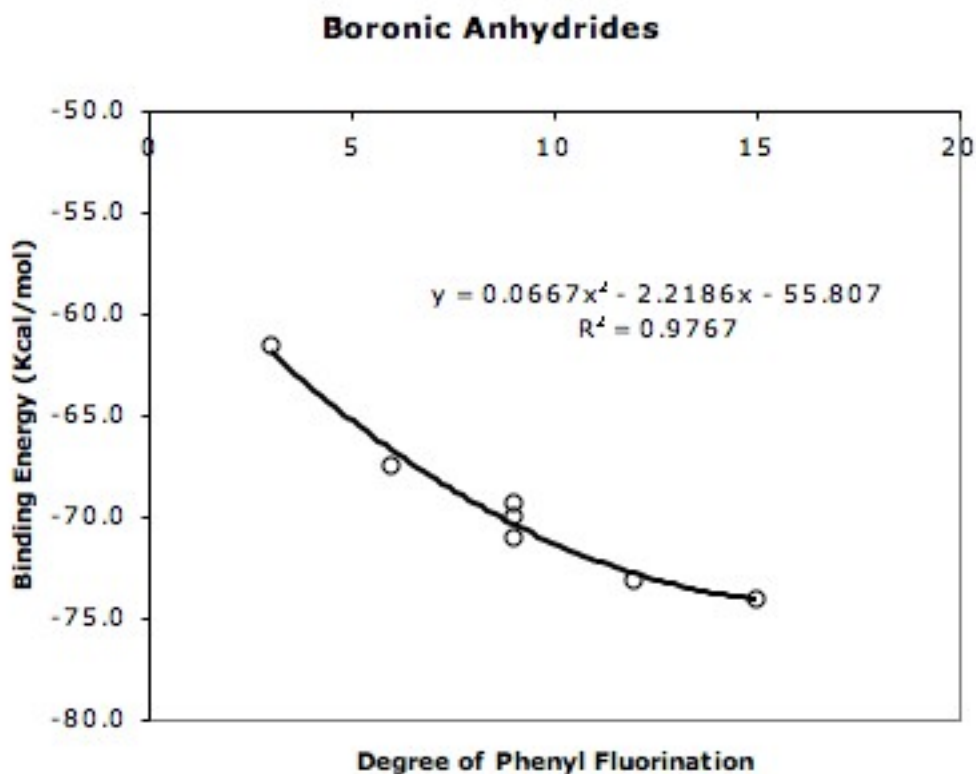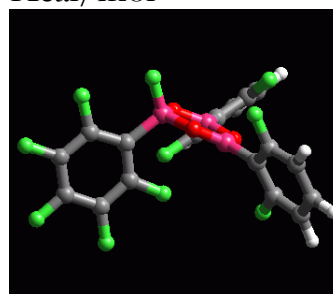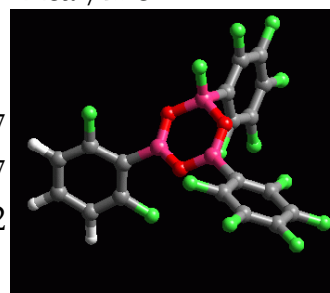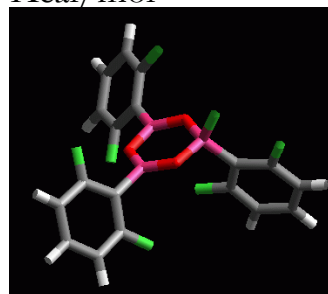
Boronic Anhydrides

$y = 0.0667x^2 - 2.2186x - 55.807$
$R^2 = 0.9767$

Binding Energy (Kcal/mol)

Degree of Phenyl Fluorination

Fig. 24. Binding energies (Kcal/mol) as a function of degree of fluorination from Quantum Mechanical (DFT) calculations on fluorinated phenyl boronic anhydrides.

The figures at the end of this report show some representative quantum calculated structures for

carb-b3lyp-udft lacvp**	Hartrees
D0P3	
PFBBA.out:	-2483.8744
PFBBAF.out:	-2583.9019
F-	-99.909472
Binding Energy	-74.1 Kcal/mol

D3P0	
DFBBA.out:	-1590.9178
DFBBAF.out:	-1690.9347
F-	-99.909472
Binding Energy	-67.5 Kcal/mol

D1P2	
D1P2.out:	-2186.2237
D1P2F.out:	-2286.2497
F-	-99.909472
Binding Energy	-73.12 Kcal/mol

D2P1	
D2P1.out:	-1888.5716
D2P1F.out:	-1988.5943
F-carb-b3lyp-udft.out lac	-99.909472
Binding Energy	-71.03 Kcal/mol
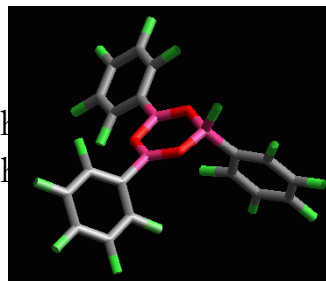
the fluorinated complex A:F- in each case.Provided there is continuing funding we could in the near future undertake the computation of related boronic anhydrides, such as fluorinated methyl, methoxy, and isopropyl boronic acid anhydrides as well. This will provide for a significant number of new anion receptors which are easy to synthesize from existing available materials.

Modeling Results on Non-Phenylated Boronic Anhydrides

Most boronic acids readily undergo dehydration to form the cyclic trimeric anhydride (boroxine; 1,3,5,2,4,6-trioxatriborinane). These are easy to manufacture in good yields. Additionally, a variety of starting materials exists that can lead potentially to a significant number of receptors with a wide range of performance. To guide the effort in search of new chemistries we report theoretical estimates of thermodynamics of new classes of fluoride anion receptor: condensation products of non-phenylated boronic acids. Previously we reported results for phenyl containing anhydrides with various degrees of fluorination, including mixed fluorination states. Here we focus our attention on other useful chemistries and present a new measure of performance that might be of significantly more use in identifying promising anion acceptors for high specific energy Lithium-Fluoride batteries.

Method

We calculated thermodynamic data in the form of electronic energies, solvation free energies in propylene carbonate, and binding energetics using Quantum Mechanical Density Functional Theory (B3LYP) for reactions of fluoride anion binding to various boronic anhydride anion receptors. We use an open shell calculation (UDFT) with a good level basis set (LACVP**) which translates to 6-31 G** basis for main group elements.

The anion receptors studied here can capture fluorine anions to form a negatively solvated anion:

$$[AR]_{solv} + [F-]_{solv} \rightarrow [AR:F(-)]_{solv} \tag{1}$$
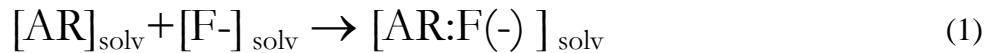
We use the term "binding energy" to refer to the free energy for this reaction. This binding energy includes electronic and also solvation effects, changes in solvation energy upon binding. Solvation effects are estimated using a Poisson-Boltzmann solver to estimate re-organization energies within the quantum mechanical DFT estimations of electronic energies.

Results

Table V presents results for five proposed boronic anhydrides. Their structures, in the anion captured form, are presented at the end of this report. We include the solvation free energy of the anion receptor in the neutral and charged forms, the binding energy, average Boron and Fluorine charges (neutral and charged states), the degree of fluorination, and the performance ratio q proposed below.

Discussion

Previously we have compared these binding energies to actual battery performance. We have concluded that a mid-range value (on the range from -68 Kcal/mol to -72 Kcal/mole) is most favorable. No precise justification has been given, other than to acknowledge that weaker binding might not be sufficient to break the LiF crystal formation energy and too strong binding might not be able to free the F- anion for electrode intercalation. We reported that upon inspection the A:F-, single capture anion receptors, show that the binding energy depends quadratically on the degree of fluorination, higher binding energies (more negative, more favorable binding) correspond to higher degrees of fluorination on the phenyl groups.

More recently it has come to our attention that the task of finding anion receptors that are soluble in propylene carbonate is a very challenging task. Thus, here we propose that as a measure of "theoretical" predicted the Solvation Free energy of Neutral Anion Receptor be taken into account. A more soluble receptor in propylene carbonate might offer an advantage. This, together with a moderate binding energy should give a good balance of properties.

Conclusions and further work:

The anion receptor candidates included here have the following order of performance, according to a balance of moderate binding energy and high solvation energy of the neutral form

tris(hexafluoroisopropylanhydride) >
tris(trifluoromethoxyanhydride)   >
tris(trifluoroaceticanhydride)   >
tris(trifluoromethylanhydride)   >
tris(methylanhydride)

Once we have experimental data on the cathode specific capacities for these proposed boronic anhydrides we can validate further this hypothesis and fine tuned the search for more effective anion receptors.

Table V: Binding energetics of various fluorinated boronic acid anhydrides and performance values (q) (last column).

| Anion Receptor	Electronic Energy Hartrees	Solvation Free Energy Kcal/mol	Binding Energy Kcal/mol	Average Boron Charge (e)	Average Change Boron (e)	Bound F-Charge (e)	Degree of Fluorination	q= Solvation/ Binding
tris(hexafluoroisopropylanhydride)	-2668.26	-31.49	-76.18	0.5966	-0.0010		18	0.41
tris(trifluoroaceticanhydride)	-1879.22	-32.24	-92.52	0.6218	-0.0298		9	0.35
tris(trifluoromethoxyanhydride)	-1539.27	-17.89	-84.14	0.6070	-0.0384		9	0.21
tris(trifluoromethylanhydride)	-1313.42	-16.56	-95.36	0.4259	-0.0456		9	0.17
tris(methylanhydride)	-420.33	-6.70	-62.68	0.4124	-0.0126		0	0.11
tris(hexafluoroisopropylanhydrideF)	-2768.29	-49.75		0.5956		-0.3821	19	0.41
tris(trifluoroaceticanhydrideF)	-1979.27	-52.86		0.5920		-0.2754	10	0.35
tris(trifluoromethoxyanhydrideF)	-1639.32	-53.25		0.5686		-0.3456	10	0.21
tris(trifluoromethylanhydrideF)	-1413.48	-49.92		0.3803		-0.3131	10	0.17
tris(methylanhydrideF)	-520.34	-59.11		0.3997		-0.3969	1	0.11
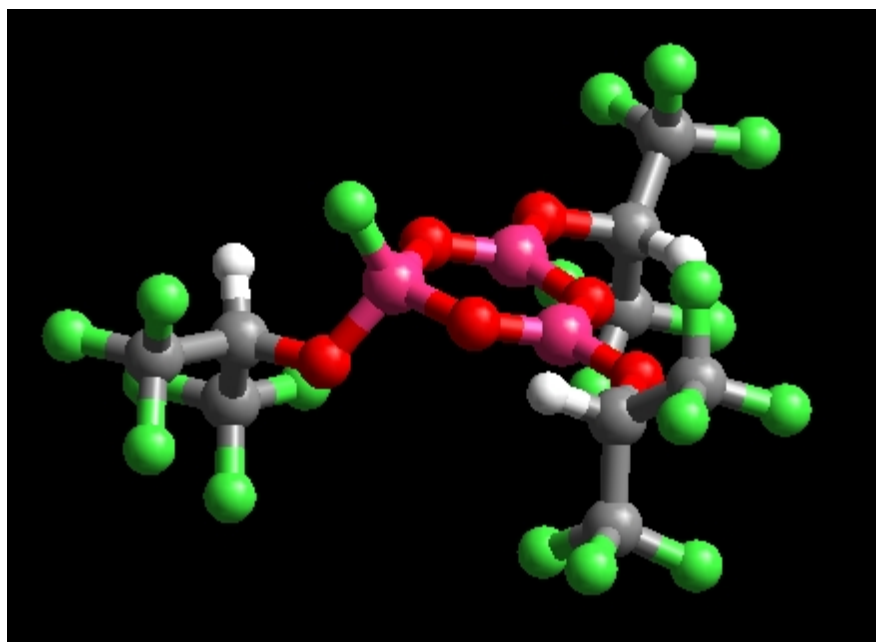
Fig 25. tris(hexafluoroisopropylanhydride). Pink=Boron, Red=Oxygen, Grey=Carbon, White=Hydrogen, Green=Fluorine Atoms.
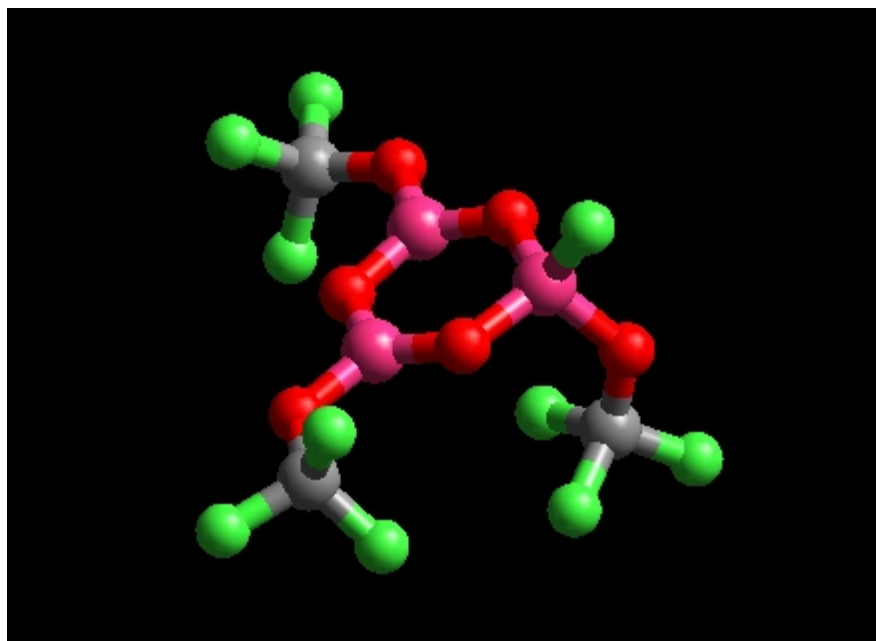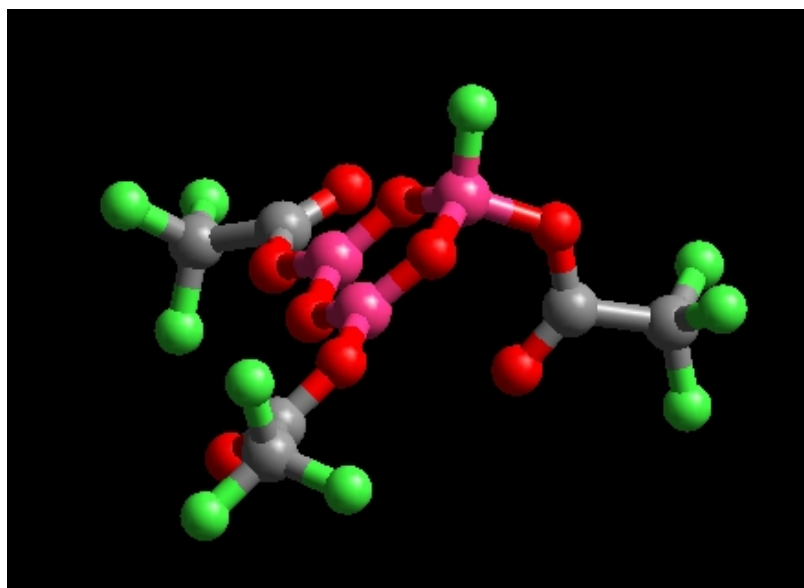

Fig 26. tris(trifluoromethoxyanhydride)
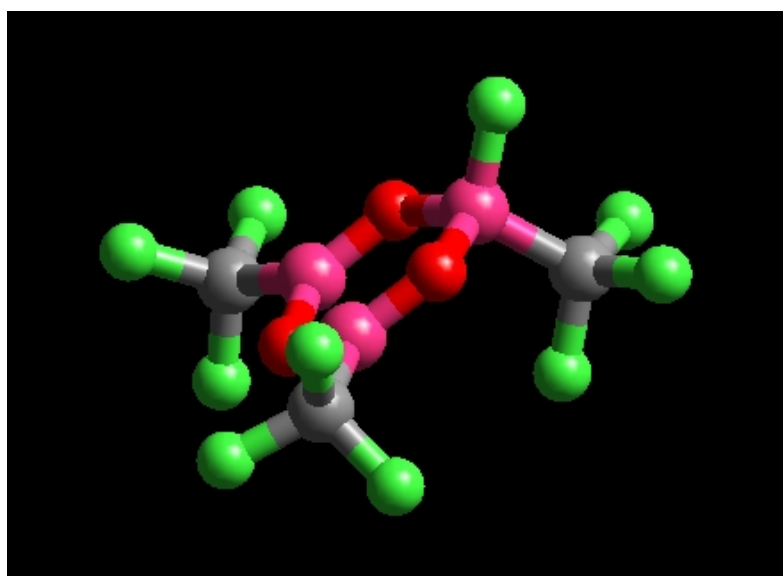
Fig. 27. tris(trifluoroaceticanhydride)

Fig. 28. tris(trifluoromethylanhydride)
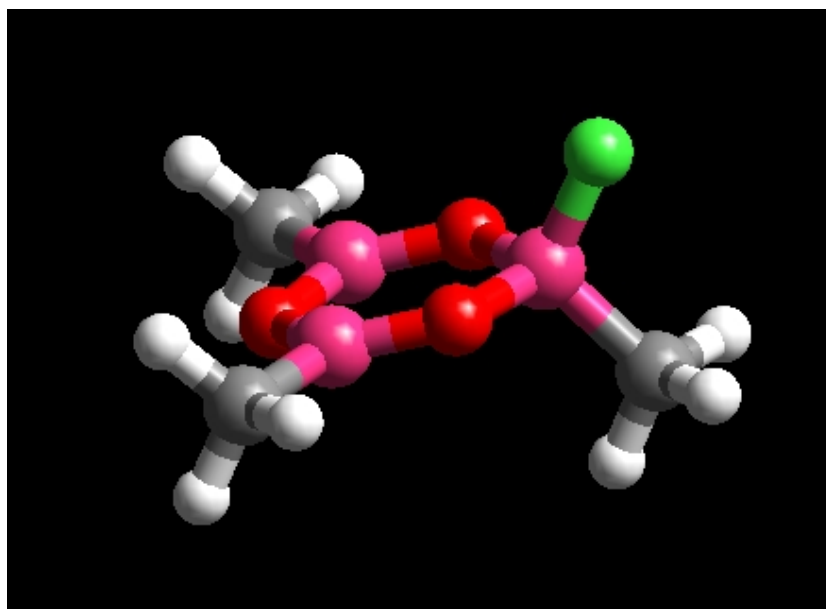
Fig. 29. tris(methylanhydride)

Binding Energy upon Dimerization

	Solvation	
TTFBA DIMER LACVP** UDFT B3LYP		
TTFBA-TTFBA-ring.out:	-2154.619179	-5.949
TTFBA/TTFBAF-TTFBA.out:	-2254.672596	-40.9228
F-carb-b3lyp-udft.out lacvp**	-99.90947179	

Binding Energy   **-90.33** Kcal/mol

Presentations and Publications

1. **Invited Talk:** "First Principles Hierarchical Selection and Testing of Anion Receptors for High Specific Energy Lithium-Fluoride Batteries", *Georgia Institute of Technology Materials Council Seminar Series, Atlanta, GA, December 2007.*
2. Designing and Testing Anion Receptors for High Specific Energy Lithium-Fluoride Batteries", W. C. West, M. Blanco, B. V. Ratnakumar, and V. R. Prakash, *Focused Battery Technology Workshop, February 2008, Pasadena, CA.*
3. "Cyclic Fluorinated Boronic Acid Anhydride Anion Receptors", W. C. West and M. Blanco, *New Technology Report # 46141,* (2008).