

Development of Tetraarylphosphonium/Tetrakis (pentafluorophenyl) borate (TAPR/TFAB) salts as non-aqueous electrolytes for organic redox flow batteries

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Abstract

A series of weakly coordinating cations/anions (TAPR/TFAB) ion pairs are, herein, being proposed as non-aqueous electrolytes for high capacity ORFBs. These were accessed via a Palladiumcatalyzed approach followed by the simple filtration/isolation of the product. These substituted tetraarylphosphonium/tetrakis(pentafluorophenyl)borate salts 1-4 where the substituents are a p-methoxy (1), a 3,4-dimethoxy (2), a p-phenyl (3), and a p-trimethylsilylacetylene (TMSA) (4) have potential use in several industries owing to their unique solubility in low polarity solvents. These salts constitute a new class of molecular ion pairs which can promote charge dissociation even in low polarity solvents because of their large size and bulkiness. The result being an increased conductivity in those media that can be useful for electrochemistry, advances in catalysis, battery technology, petroleum handling etc. This work supports the national security goal of fostering the development of affordable, clean and renewable energy source and storage.

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Development of Tetraarylphosphonium/Tetrakis (pentafluorophenyl) borate (TAP^R/TFAB) salts as non-aqueous electrolytes for organic redox flow batteries

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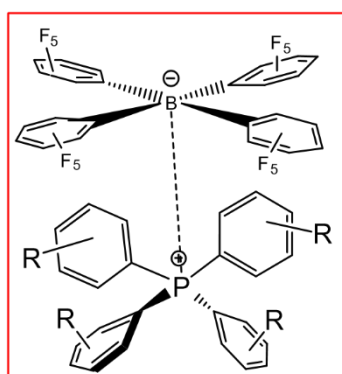
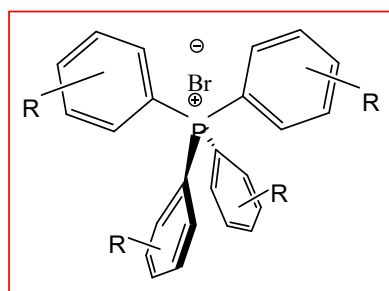
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ABSTRACT

A series of weakly coordinating cations/anions (TAP^R/TFAB) ion pairs are, herein, being proposed as non-aqueous electrolytes for high capacity ORFBs. These were accessed via a Palladiumcatalyzed approach followed by the simple filtration/isolation of the product. These substituted tetraarylphosphonium/tetrakis(pentafluorophenyl)borate salts **1-4** where the substituents are a p-methoxy (**1**), a 3,4-dimethoxy (**2**), a p-phenyl (**3**), and a p-trimethylsilylacetylene (TMSA) (**4**) have potential use in several industries owing to their unique solubility in low polarity solvents. These salts constitute a new class of molecular ion pairs which can promote charge dissociation even in low polarity solvents because of their large size and bulkiness. The result being an increased conductivity in those media that can be useful for electrochemistry, advances in catalysis, battery technology, petroleum handling etc. This work supports the national security goal of fostering the development of affordable, clean and renewable energy source and storage.

GRAPHICAL ABSTRACT



(1) R= pOMe (2) R= 3,4-diOMe

(3) R=pPh

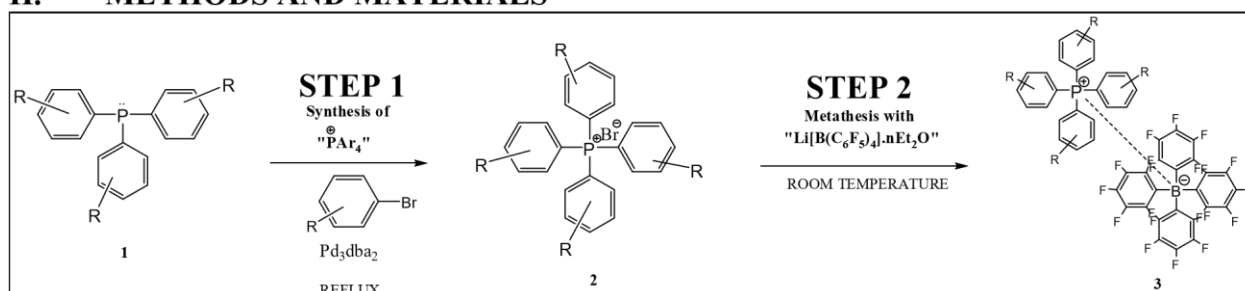
(4) R= pTMSA

I. INTRODUCTION

The need for improving the electrical grid with clean renewable energy sources cannot be overstated.¹⁻³ One solution is the development of Organic Redox Flow Batteries (ORFBs) as these have become of great interest due to their higher voltage and higher current density than existing aqueous systems. Non-aqueous flow batteries are becoming a viable alternative to their aqueous counterparts. Not only are they cost efficient since they can be generated from an abundance of starting materials, non-aqueous redox flow batteries also offer the opportunity for increasing cell potentials because of the larger electrochemical windows that exist with organic molecules and solvents in terms of solubility, chemical reactivity, and redox potentials.⁴ The performance of a battery is contingent to the selection and performance of electrolytes. Weakly coordinating cations and anions (WCCs/WCAs) are proposed in this work because these species are known to be soluble in low polarity solvents.⁵ Weakly coordinating anions such as tetrakis(pentafluorophenyl)borate are widely studied as electrolytes in catalysis, for lithium-ion batteries, and in electrochemistry.⁶⁻⁷ However, reports of their electrochemical use as supporting electrolytes in non-polar environments are scarce. Recently, Mullen and Floudas have developed a novel class of weakly coordinating anions and cations by polyphenylene-dendrimerizing of tetraarylborate ions and tetraphenylphosphonium ions, respectively.⁸⁻¹¹ Our preliminary data indicate that we have successfully synthesized a series of WCCs/WCAs or tetraarylphosphonium/tetrakis(pentafluorophenyl)borate (TAP^R/TFAB), one of which produced conductivity data shown to approach the automotive industry leading electrolytes in terms of stability and limiting conductivity.¹² Thus the impetus to design and study further TAP^R/TFAB salts and to probe coordination in ion-pairing through the determination of association constants and redox potentials.

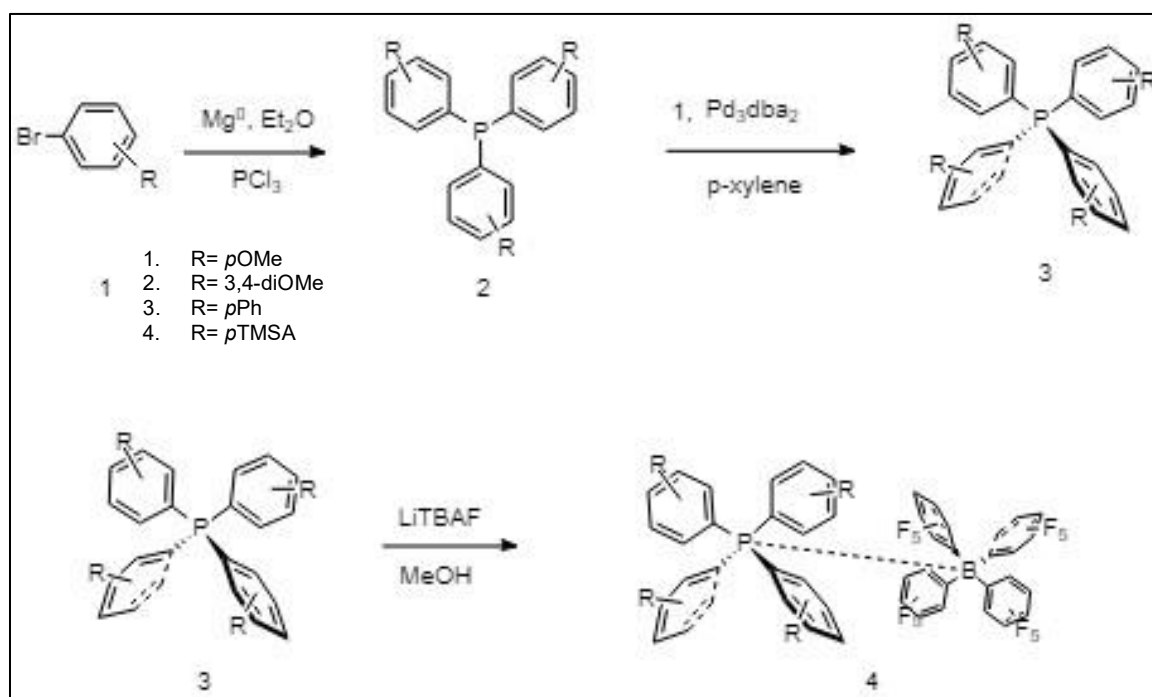
The specific goal of this project is the synthesis of a series of electrolytes bearing various electron donating functional groups (salts **1-4**) and examine how the substituents introduced in tetraarylphosphonium ions (cations) affect the ion association/disassociation in electrolytes. We have shown that electron donating groups in aryl groups make the central positive charge more delocalized in peripheral aryl groups, thus enhancing the cation-anion disassociation which this research project aims to measure. Specifically, we will 1) check the stability of salts **1-4** in electrochemistry relevant conditions, assessing electrochemical windows of solvents and electrolytes combinations, 2) perform conductivity measurements to obtain association constants in non-polar solvents. We hypothesize the successful design of weakly coordinating cation-anion electrolyte pairs (WCC-A) will provide enough steric hindrance to lower the association constants, and therefore the impact of ion pairing, between the electrolyte cation and analyte radical anion.

II. METHODS AND MATERIALS



Scheme 1: Synthesis of TPA^R-TFAB from commercially available aryl halides.

As depicted in the general Scheme 1, substituted aryl halides underwent a palladium-catalyzed coupling reaction with corresponding triarylphosphines **1** in boiling *p*-xylene in order to yield novel substituted tetraarylphosphonium ylides **2**. The insoluble phosphonium bromide precipitated in *p*-xylene and was isolated from the reaction media by simple filtration. The subsequent metathesis reaction allowed an exchange of ions between the phosphonium ylide **2** and the lithium tetrakis(pentafluorophenyl)borate (LiTFAB) salt, which resulted in the formation of lithium bromide and the desired ion-pair tetraarylphosphonium(TAP)-TFAB **3**. Experiments were carried out under inert gas atmosphere using Schlenk conditions, and anhydrous solvents were used wherever indicated. Chemicals were used as received (Aldrich, anhydrous). Preparation of these Wittig salts followed a modified procedure by Charette et al.¹³ Synthesized compounds were characterized by NMR spectroscopy using a state-of-the-art Bruker Avance 400MHz.

**Scheme 2: Synthesis of TPA^R-TFAB with a Grignard reaction of the aryl halide 1.**

Magnesium was refluxed with aryl halide **1** in a facile Grignard reaction with phosphorous trichloride and anhydrous ethyl acetate. The reaction was flushed in argon gas then vacuum filtered to provide phosphine **2** in high yield. The phosphonium ylide **3** was synthesized via a Pallidum cross-coupling reaction of phosphine **2** and aryl halide **1** and refluxed in boiling *p*-xylene. The reaction mixture was then vacuum filtered and rinsed with acetone. The phosphonium ylide underwent metathesis by LiTFAB in methanol. The mixture was refluxed in a water bath at ~70°C. The TAP^R-TFAB **4** pair was yielded by simple filtration. All synthesized compounds were characterized by ¹H NMR and a provisional ¹³C NMR was also obtained whenever possible.

A YSI 3200 Conductivity Meter with a model 3265 flow cell was used to take the conductivity measurements of all TAP^R-TFAB pairs. Lee Wheaton curve fitting function was used to determine both K_a and Λ_0 values. Igor was used to analyze all of the data.

III. RESULTS AND DISCUSSION

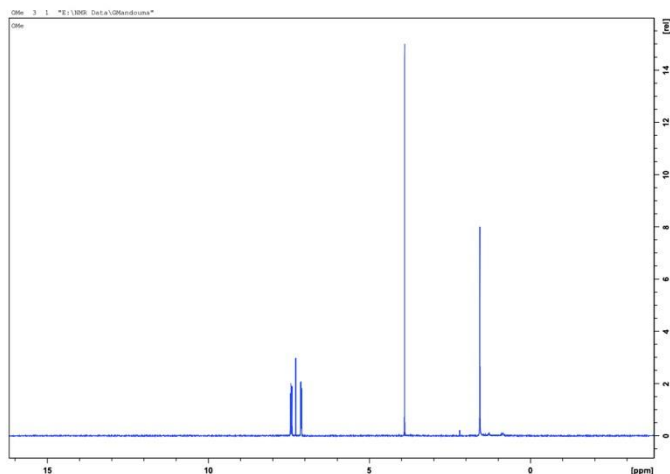


Figure 1: ^1H NMR of $\text{TA}^{\text{OMe}}\text{P}/\text{TFAB}$ salt.

In **Figure 1**, the proton NMR of salt **1**, reveals the two aromatic doublets and the methoxy singlet at 3.84ppm in the proton NMR. The ^1H NMR shows a pattern similar to the phosphonium with significant shift upfield (7.45ppm and 7.1ppm) as the bromide was replaced by the Boron-bearing TFAB anion. The synthesized tetraphenylphosphonium bromide is depicted in **Figure 1**.

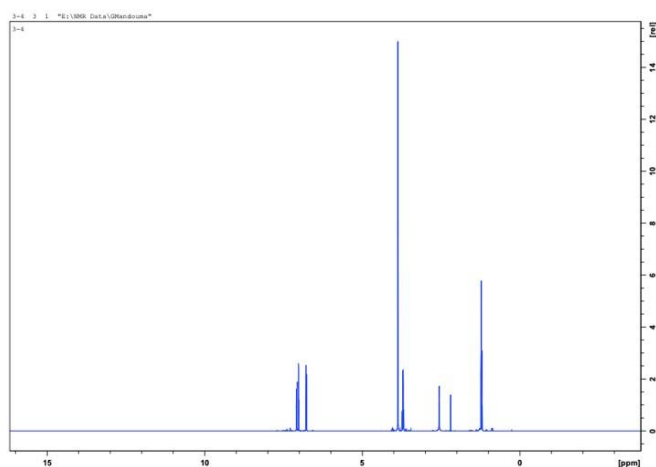


Figure 2: ^1H NMR OF $\text{TA}^{3,4\text{-diOMe}}\text{P}/\text{TFAB}$ salt.

In **Figure 2**, the substituent used was $\text{R}=3,4\text{diOMe}$ and the ^1H NMR depicts the methoxy group as a singlet at 3.84 ppm. The spectra shows the two aromatic protons between 6-7.5ppm (d,2H) (t, 3H).

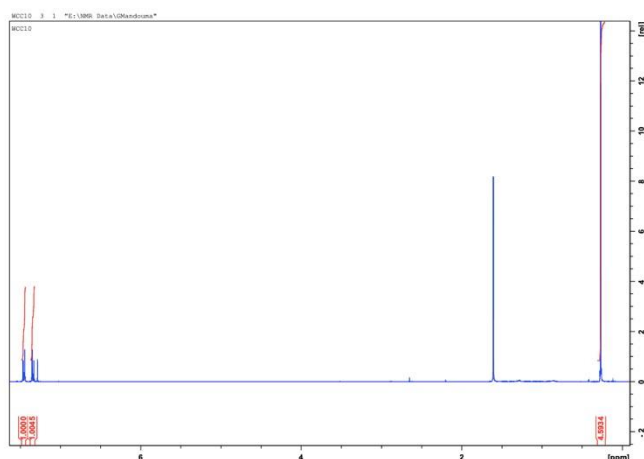


Figure 3: ^1H NMR OF $\text{TA}^{\text{TMSA}}\text{P}/\text{TFAB}$ salt.

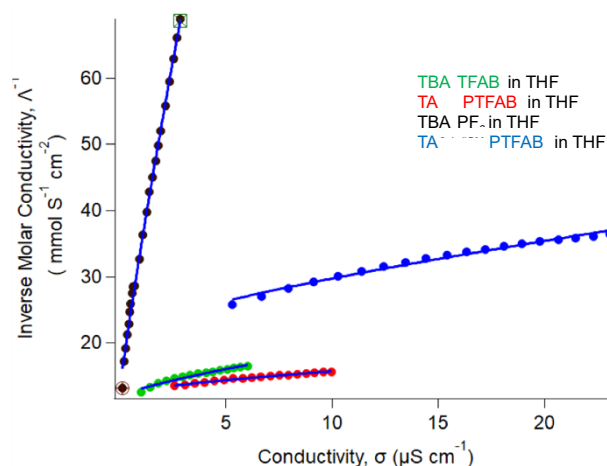


Figure 4: Inverse molar conductivity versus conductivity of data for $\text{TBA}^+\text{PF}_6^-$, $\text{TBA}^+\text{TFAB}^-$, $\text{TA}^{\text{OMe}}\text{PTFAB}$, and $\text{TA}^{3,4\text{-diOMe}}\text{PTFAB}$ in THF.

The reduction in K_A from TBA^+ to $\text{TA}^{\text{OMe}}\text{P}^+$ (both with TFAB^-) in THF is promising as it suggests success in designing $\text{TA}^{\text{OMe}}\text{P}^+\text{TFAB}^-$ to be a WCC-A pair less capable of ion pairing. A decrease in the K_A value is seen in the TBME conductivity tests, further supporting the idea that $\text{TA}^{\text{OMe}}\text{P}^+\text{TFAB}^-$ is more weakly coordinating than $\text{TBA}^+\text{TFAB}^-$.

Indeed, non- and low-polar solvents can be made sufficiently conducting when these weakly coordinating anions/cations are dissolved in the solvent.⁹ Ions associate in solution to form a stable entity in media of low permittivity because coulombic interactions are greater than the thermal energies of the “separated” ions.¹⁰ Bjerrum postulated that ions of opposite charges within a certain distance of one another will associate if the critical ion capture distance q is greater than the distance r between the two ions.

In Figure 3, the trimethylsilylacetylene of salt 4 proton is displayed at 0.25. The two aromatic doublets and the methoxy singlet at 3.84ppm in the proton NMR. The $\text{TA}^{\text{OMe}}\text{P}^+\text{TFAB}^-$ was obtained after metathesis reaction of the corresponding phosphonium bromide with LiTFAB . The ^{19}F NMR is displayed in Figure 6 showcasing the presence of the fluorine atom.

We performed electrochemical experiments to probe the effect of both the solvent and the synthesized electrolytes TAP-TFAB ionpairs 1 and 2 on conductivity in low-polar media (THF and TBME). Data for $\text{TA}^{\text{OMe}}\text{P}^+\text{TFAB}^-$ in THF (Fig. 4) correlate well with preliminary data: values for Λ_0 and K_A were $90.1 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ and 4.37×10^3 .¹² In TBME, the value for Λ_0 , like $\text{TBA}^+\text{TFAB}^-$ in TBME (Fig. 5), was lower than predicted by

the Walden product ($113 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$), likely for the same reason as $\text{TBA}^+\text{TFAB}^-$ in TBME.

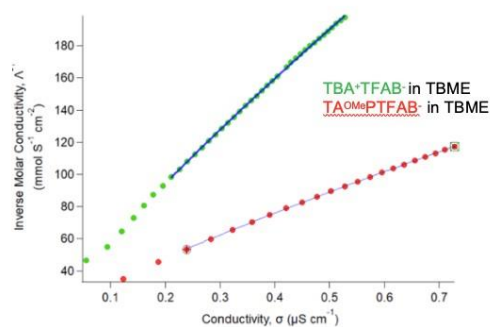


Figure 5: Inverse molar conductivity versus conductivity

of data for TBA/TFAB AND $\text{TA}^{\text{OMe}}\text{P}/\text{TFAB}$ in TBME.

also

TAP ^R -TFAB Substituents	Disassociation Constant (K _d)	Limiting Conductivity (Λ ₀)	Association Constant (K _a)
R= <i>p</i> OMe	3.03 x 10 ⁻⁴	78.6 Scm ² /mole	3.30 x 10 ³
R=di-3,4-OMe	4.15 x 10 ⁻⁴	49.1 Scm ² /mole	2.41 x 10 ³
TBA-TFAB	1.63 x 10 ⁻⁴	86.2 Scm ² /mole	6.15 x 10 ³
TBA-PF ₆	2.86 x 10 ⁻⁶	86.2 Scm ² /mole	373.13 x 10 ³

Table 1. Conductivity data for TAP^R-TFAB salts.

These conductivity results show that the highest limiting conductivity of the synthesized salts belongs to TAP^R-TFAB **1** (R=*p*OMe) at 78.6 S/m which is closest to TBA-PF₆, the leading industrial supporting electrolyte.

IV. CONCLUSION

Electrolytes in Lithium ion batteries are solutions whose function is to ferry Li⁺ ions between the electrodes. Their most important properties are stability (both thermal and hydrolytic) and high conductivity. Then, they must also display high discharge rate and good performance at both high and low temperatures. In addition, good electrolytes should not be conducive to overcharging of the Li-ion batteries. A certain advantage to WCC's/WCA's **1-4** and others being developed is their increased solubility in organic solvents, above inorganic salts LiPF₄ and LiPF₆ commonly used in Li-ion batteries.¹⁴ Since a WCC's/WCA's high solubility correlates to its high conductivity, we have described the synthesis of compounds that constitute a novel class of potential electrolytes which stand to play an important role in meeting the demand of future Organic Redox Flow Batteries batteries because of their exceptionally high conductivities, in low polarity solvents, in the results described herein. Further fine-tuning of the substitution pattern in the aromatic rings will be conducted to examine its effects on the upper limit of ion dissociations and conductivity. Increasing the size and bulkiness of the cation correlates well with a decrease in ion-pairing and, therefore, an increase in limiting conductivity of the ion-pair in low-polarity solvent. In this respect, we plan to consider bulkier substituents R= biphenyl and R= terphenyl in an effort to attain even higher limiting conductivities in low-polarity solvents.

The current project addresses the goal of diversifying the nation's sources of renewable energy and storage thereof. The performance of Li-ion battery is contingent to the selection and performance of electrolytes. In TAP^R-TFAB, we are developing electrolytes for the future which could impact the nation's renewable energy map. These compounds have been successfully synthesized and conductivity measurements have shown that they are comparable (especially TAP^R-TFAB **1** (R=*p*OMe)) to leading electrolytes in the automotive industry in terms of limiting conductivity. Furthermore, these compounds can be used to probe coordination in ion-pairs through DOSY NMR and the determination of association constants and redox potentials.

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