

Review

Boron based fluoride anion receptors: Electrochemical and sensory applications

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ABSTRACT

Boron based fluoride anion receptors as electrolyte additives would significantly improve lithium ion battery performance. Fluorinated versions of triarylboranes, boronate esters, boroxines, and other boron based anion receptors have potential applications in the design of high specific energy lithium ion batteries. There is also an emerging interest in recent years in the design of colorimetric sensors for the fluoride anion, especially in aqueous systems, using boron based anion receptors. This mini review highlights the recent trends in the design and applications of the boron based fluoride anion receptors as electrolyte additives and as colorimetric sensors.

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1. Introduction

Boron-based anion receptors such as tris(1,1,1,3,3,3-hexafluoropropan-2-yl) borate (TPFB), tris(pentafluorophenyl) borate (THFIPB), tris(pentafluorophenyl)borane (TPFPB) were first demonstrated by Yang, McBreen and coworkers as fluoride, oxide or peroxide anion specific receptors when used as additives in lithium ion batteries (based on LiF, Li₂O or Li₂O₂ as electrolytes in carbonate-based solvents) (Fig. 1) [1–4]. The state of the art electrolyte materials such as LiPF₆ exhibit relatively low lithium ion transference numbers, and therefore there is renewed interest to develop selective anion receptors that would facilitate enhanced dissociation of the lithium salts, thereby resulting in increased lithium ion transference numbers [5]. The dual ion intercalation secondary rechargeable lithium ion batteries using lithium fluoride salts are particularly attractive in this regard for achieving relatively high specific energy values. However, the relative insolubility of the LiF in many nonaqueous electrolyte solvents limits its use as a viable electrolyte salt, and therefore the use of the fluoride specific anion receptors as electrolyte additives is a clear alternative towards achieving enhanced solubility of LiF and thereby the

relatively increased lithium ion transference numbers [5–11].

The selective reversible binding of these boron-based anion receptors resulted in enhanced lithium ion transference numbers. For example, in the presence of 0.4 M TPFB in 0.2 M Li₂O/1:1 EC:DMC (ethylene carbonate and dimethyl carbonate solvents) the lithium ion transference number was observed to be as high as 0.89. Similarly, a lithium ion transference number of 0.74 was observed for 0.4 M TPFB in 0.2 M Li₂O₂/1:1 PC (propylene carbonate):DMC. These Li⁺ transference numbers are typically 100% higher than the values for the commonly used electrolytes in the absence of the anion receptors [2]. The enhanced Li⁺ transference numbers would result in relatively high lithium ion conductivities in lithium ion cells. The use of these anion receptors allows the use of LiF as a low molecular weight electrolyte in the lithium ion batteries. Whereas LiF is essentially insoluble in the nonaqueous electrolyte solvents such as dimethyl ether (DME) and carbonate based solvents, in the presence of anion receptors LiF is relatively highly soluble, and typically 1 M solutions of LiF in dimethyl ether could be obtained so that high lithium ion conductivities could be achieved in lithium ion batteries [1,3,4].

Whereas there are relatively highly selective colorimetric fluoride anion receptors based on Bronsted acid–base reactions or hydrogen bonding interactions as in the case of urea- [12–15], indole- [16], pyrrole- [17,18], carbazole- [19], thiourea- [20] and

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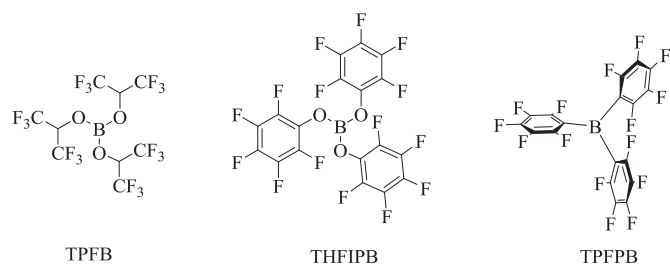


Fig. 1. Structures of a trialkoxyborane TPFB, a triaryloxyborane THFIPB, and a perfluorinated triarylborane TPFPPB.

calixarene-based [21–24] anion receptors (Fig. 2), the boron-based anion receptors have superior electrochemical and thermal stabilities, and thereby are compatible with the state of the art carbonate-based nonaqueous electrolytes ($E_{\text{ox}} > 4.5 \text{ V vs Li/Li}^+$) [25]. The borate- and boroxine-based fluoride anion receptors are readily accessible from the corresponding relatively inexpensive boric acid derivatives. Furthermore, the fluoride anion affinities of the boron based anion receptors could be reliably predicted by ab initio calculations. Amine and coworkers' ab initio calculations, for example, show that the fluoride anion affinity is reduced by the introduction of the alkoxy groups on the boron center and that the fluoride anion affinity increases with the substitution of the electron-withdrawing groups on the boron (e.g., fluoroalkyl or fluoroaryl aryl substituents on the boron) [26]. The anion receptor TPFPPB was shown also to complex with PF_6^- anion (i.e., in addition to its complexation with the fluoride anion) so that the lithium ion transference number (and thereby the ionic conductivity) of the cells consisting of LiPF_6 electrolyte are significantly increased [27].

The applications of these anion receptors and the associated electrolytes in lithium ion batteries and lithium–air batteries has been reviewed [7,25], and therefore we will only briefly address the fundamental concepts involved in their applications in lithium ion batteries and highlight the recent applications of the fluoride anion receptors. Appropriately selective fluoride anion receptors have potential impact on the commercial applications of the lithium ion and metal–air batteries.

Due to the environmental as well as toxicity effects of fluoride anions there has been renewed interest in developing analytical

techniques for the detection and quantification of the fluoride ion concentrations in aqueous and nonaqueous systems. Fluoride anion selective colorimetric sensors, in particular in aqueous systems, are highly desirable as many industrial pollutants release fluoride ions into the waste water systems. The commonly used Bronsted acid–base sensors involving urea and other amines (such as pyrrole, thiourea and guanidinium based compound)-based anion receptors are particularly useful for these applications. However, most of these Bronsted acid-based anion receptors suffer from their relatively non-selective nature towards the fluoride anion, as they also form acid–base complexes with various other anions such as acetate, dihydrogen phosphate, and other halides, exhibiting color changes. Boron-based anion receptors (Lewis acid–base complex based) are especially well suited for the selective analysis of the fluoride anion as boron has relatively superior fluoride anion affinity due to the relatively high B–F bond strengths. However, in aqueous solvents, due to the strong solvation of the fluoride anion by water, selective fluoride anion binding by the anion receptors is still a challenge. This area of fluorescence and colorimetric detection and quantitative analysis of the fluoride anions has been well reviewed, and therefore we highlight only the most illustrative recent examples of the boron-based colorimetric fluoride anion sensors [28–36]. Gabbaï and coworkers have recently reported sterically crowded triarylboranes as fluoride anion specific receptors (*vide infra*) [37–40]. In the latter cases, complementarity of the hydrogen-bonding interactions from the neighboring N–H or O–H bonds significantly enhances the fluoride anion binding (*vide infra*). A wide variety of the sterically crowded triarylboranes have been synthesized recently and investigated for their fluoride anion binding and for their potential use as colorimetric sensors (*vide infra*).

2. Cyclic boronate esters as electrolyte additives in lithium ion batteries

The sterically less encumbered cyclic boronate esters are expected to have relatively higher fluoride anion affinities in nonaqueous solvents as compared to those of their acyclic analogs. McBreen and coworkers have synthesized the perfluorinated catechol- and perfluorinated pinacol-derived borate esters of the pentafluorophenylboronic acid (4,5,6,7-tetrafluoro-2-(2,3,4,5,6) pentafluorophenyl borzodioxaborole (1) and 2-(pentafluorophenyl)-4,4,5,5-tetrakis-(trifluoromethyl)-1,3,2-dioxaborolane (2)

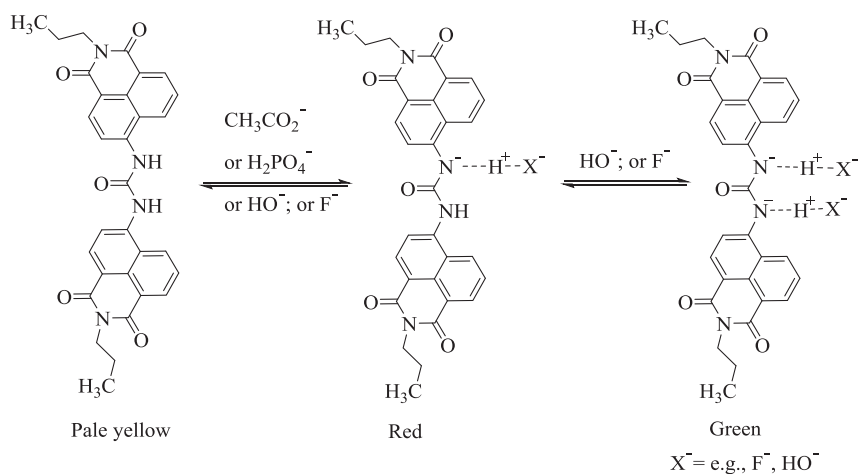


Fig. 2. Color changes upon complexation of fluoride anion by a chromogenic urea derivative; the NH bond of the urea derivative is successively, almost completely deprotonated upon addition of the tetrabutylammonium fluoride [13]. The second deprotonation step could be achieved using the fluoride or hydroxide anions, whereas other anions such as acetate and dihydrogen phosphate could only achieve the first deprotonation.

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