Organophosphorus Decorated Lithium Borate and Phosphate Salts with Extended π-Conjugated Backbone

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ARTICLE

Organophosphorus Decorated Lithium Borate and Phosphate Salts with Extended π-Conjugated Backbone

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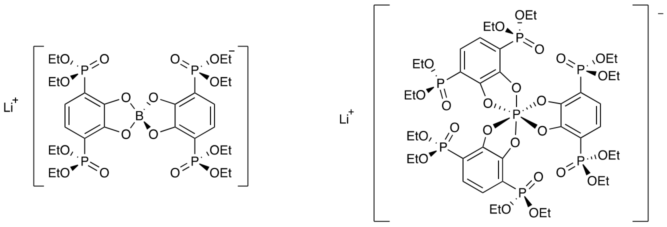
Several new bifunctional salts, **Li[B(DPN)₂]**, **Li[B(DPN)(ox)]** and **Li[P(DPN)₃],** have been prepared from the phosphorus (V)-containing chelating ligand 2,3-dihydroxynaphthalene-1,4-(tetraethyl)bis(phosphonate) (**H₂-DPN**). The new lithium salts were characterized by a variety of spectroscopic techniques. Both **H₂-DPN** and **Li[B(DPN)₂]** have been structurally characterized by X-ray crystallographic methods. These salts are related to materials being examined for use in electrolyte solutions for lithium-ion battery (LIB) applications.

Introduction

Lithium salts, such as $LiPF_6$, are an essential part of lithium-ion batteries (LIBs).[1-9] As energy demands in both personal electronics and transport applications increase, safety concerns surrounding larger scale LIBs have arisen due to a number of well-publicized battery failures and fires.[10,11] Safety concerns surrounding the fact that during catastrophic failures salts such as LiPF6 can decompose into toxic and reactive compounds.[12,13] The presence of often highly reactive materials and flammable organic solvents also present unique challenges.[14]

A wide variety of chemical and engineering strategies are currently being investigated to mitigate the risks and dangers associated with LIBs.[13-21] The inclusion of additives such as lithium salts into an electrolyte system has been explored as means to help alleviate the dangers in LIBs. These additives can be used as flame retardants to target the problem without compromising battery performance.[13,22-28] One strategy for mitigating the risks of LIBs involves developing new form of lithium salts used in electrolyte systems of batteries.

Our past work on bifunctional flame-retardant Ions (FRIONs) incorporates select phosphorus (V) flame-retardant moieties within the structural backbone of the anion of lithium salts.[29,20] This class of materials involved the synthesis of lithium salts containing a chelating organophosphorus entity, *i.e.* tetraethyl diphosphinato catechol (DPC). These salts, seen in Chart 1, utilize the chelating DPC ligand around either a boron or phosphorus atom center.[29,30]



Li[B(DPC)$_2$] Li[P(DPC)$_3$]

Chart 1. DPC FRIONs.

These two potential FRIONs represent tetra- and hexa-{P=O(OEt)$_2$} substituted (decorated) analogues of Li[B(cat)$_2$] and Li[P(cat)$_3$] that have been studied as electrolytes.[11,27,31–43] In the course of our work, the pK_a for the H$_2$-DPC ligand was experimentally determined to be 5.41, a value similar to tetrachlorocatechol (pKa = 5.83).[44] The pKa similarity between DPC and tetrachlorocatechol experimentally verifies the electron withdrawing properties of the phosphoryl group on aromatic diol systems. The addition of these electron withdrawing groups increases the anodic stability by charge delocalization in turn granting electrochemical stability, making organoborate salts suitable for LIB applications.

Another interesting class of lithium salts encompasses chelating organoborate salts including lithium bis[2,3-naphthalenediolato(2-)-O,O']borate, (Li[B(nat)$_2$]), which was prepared for use as a non-aqueous electrolyte in LIBs.[42,44] Utilizing an extended π-conjugated backbone has been previously found to offer electrochemical stability to anion salts.[45] The anodic stability was also extended by the addition of electron withdrawing groups (ca 0.1 V/fluorine atom) to the aromatic backbone of the chelating ligand.[44] For this present study, the synthesis of the tetra-{P=O(OEt)$_2$} functionalized

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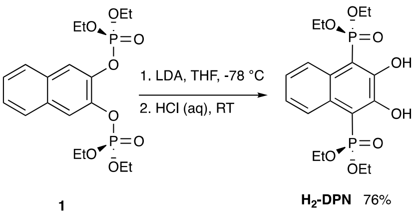


Scheme 1. Preparation of **H_2-DPN**.

analogue of Li[B(nat)$_2$] was sought, so to examine the generality of these types of lithium salts containing electron withdrawing phosphoryl groups combined with an expanded aromatic π-conjugated ring system. A DPN analogue of Li[P(DPC)$_3$] is also reported.

Results and discussion

The new chelating ligand 2,3-dihydroxynaphthalene-1,4-(tetraethyl)bis(phosphonate) (**H_2-DPN**) was readily prepared from commercially available 2,3-dihydroxynaphthalene in two steps. Reaction of 2,3-dihydroxynaphthalene with 2 equivalents of diethylchlorophosphate in the presence of triethylamine affords the necessary precursor 2,3-naphthelene(tetraethyl)bisphosphate (**1**) in good yields (75.8%).[29] Application of the anionic phospho-Fries rearrangement[46]using LDA as the base results in rearrangement of the phosphorus group of **1** to produce **H_2-DPN** in 76% yield after workup. This transformation is confirmed by the observation of a downfield shift of the ^{31}P{^{1}H} signal of **1** from δ = -6.5 ppm to δ = 23.7 ppm. Slow evaporation of a methanol solution of **H_2-DPN** yields white crystals suitable for analysis by single crystal X-ray diffraction methods, and the resulting structure of **H_2-DPN** is presented in Figure 1. The most notable features of this compound are the presence of a pair of intramolecular hydrogen bonds between the phosphoryl oxygens and vicinal hydroxyl hydrogen atoms ($d_{O\bullet\bullet\bullet HO}$ = 1.754, 1.748 Å). The packing structure for **H_2-DPN** does not reveal any significant intermolecular interactions, unlike the previously reported **H_2-DPC** analogue.[29]

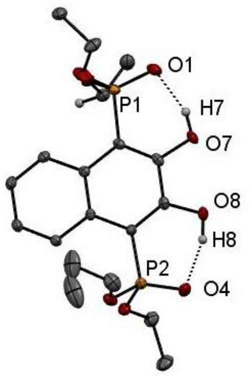
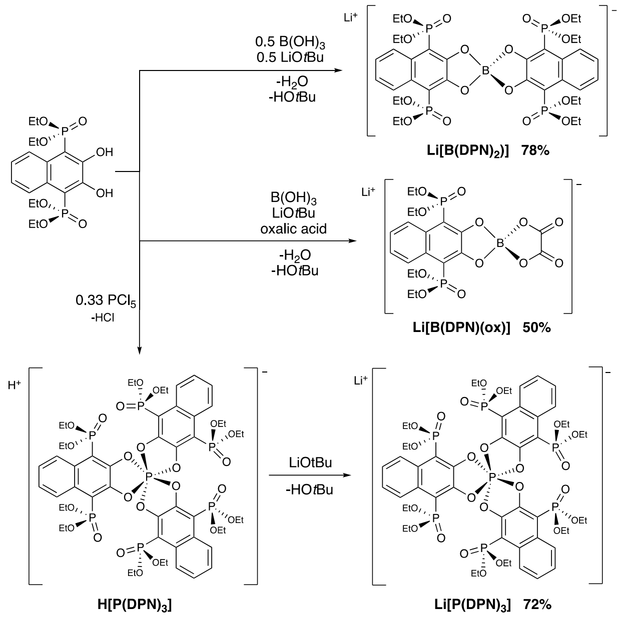


Figure 1. ORTEP diagram (50% probability level) for **H_2-DPN**. Hydrogen bonding indicated by dotted lines. Hydrogens that are not participating in hydrogen bonding omitted for clarity.



Scheme 2. Conversion of **H_2-DPN** into lithium salts.

Reaction of two equivalents of **H_2-DPN** with one equivalent of boric acid and lithium *t*-butoxide in refluxing toluene leads to the salt **Li[B(DPN)$_2$]** as a white powder in 78% yield after filtration and drying (Scheme 2). The ^{31}P{^{1}H} spectrum (DMSO-d_6) for **Li[B(DPN$_2$)]** presents a resonance at δ = 16.8 ppm which is similar to that of previously reported catechol based FRIONs **Li[B(DPC)$_2$]** and **Li[P(DPC)$_3$]** (δ = 16.4, δ = 10.7 ppm, respectively). The ^{11}B NMR chemical shift for **Li[B(DPN$_2$)]** is located at δ = 14.3 ppm, which is slightly downfield of the corresponding signal for **Li[B(DPC$_2$)]** (δ = 11.8 ppm).[29]

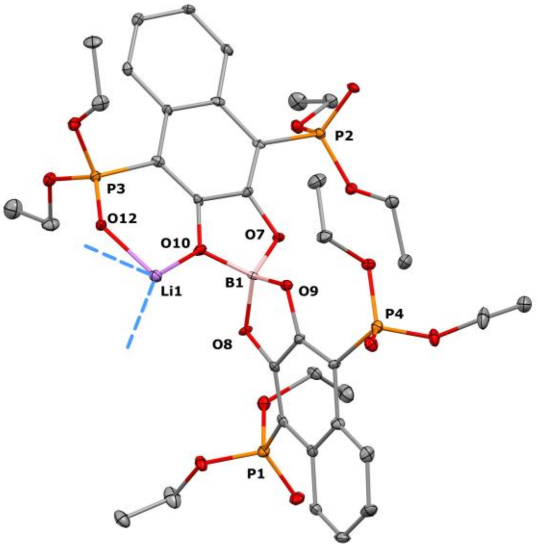


Figure 2. ORTEP diagram (50% probability level) for one of two independent molecules of **Li[B(DPN)$_2$]**, hydrogens omitted for clarity.

Furthermore, it is similar to the previously reported lithium bis-(2,3-dihydroxynaphthalene)borate Li[B(nat)$_2$] which has a chemical shift of δ = 13.0 ppm.[42]

White crystals of **Li[B(DPN)$_2$]** suitable for analysis by X-ray crystallography were obtained by the layering of ethyl acetate over a concentrated methanol solution of **Li[B(DPN)$_2$]**. Figure 2 displays one of these independent units. Within the crystals of **Li[B(DPN)$_2$]** are two essentially identical independent molecules, bridged by two lithium ions via Li•••O=P interactions. Each lithium atom is tetrahedrally coordinated by oxygen atoms, three sites by oxygens of phosphoryl groups from three different DPN anions, and by one oxygen atom from a B-O bond. The **Li[B(DPN$_2$)]** salt assembles into an extended tubular array in the solid state (Figure S20).

Electrochemical inertness is a desired property of electrolyte salts. Cyclic voltammetric studies of **Li[B(DPN$_2$)]** (Figure 3) were thus undertaken. These experiments were performed inside a glovebox under N$_2$ with a glassy carbon (3 mm) working electrode, a non-aqueous Ag/Ag$^+$ reference electrode and a Pt (2 mm) counter electrode with a scan rate of 0.08 V/s. The supporting electrolyte solution contained 0.1 M tetrabutylammonium hexafluorophosphate ([Bu$_4$N][PF$_6$]) in distilled dichloromethane (DCM). The concentration of the analyte in the electrolyte was 0.1 mM and 0.1 mM ferrocene was used as a standard. Under these conditions no significant redox activity was observed at the electrode surface for **Li[B(DPN)$_2$]**. This suggests that phosphorylation of the naphthalene diol, similar to other electron withdrawing groups, retains the very wide electrochemical window of the borate salt, keeping it viable as an electrolyte material for LIBs.

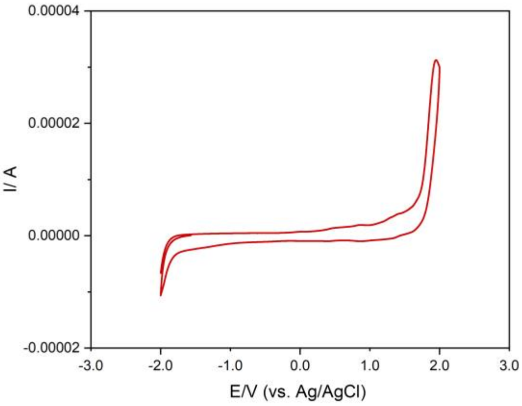


Figure 3. Cyclic Voltammogram of **Li[B(DPN)$_2$]** (0.1 mM); [Bu$_4$]NPF$_6$ (Tetrabutylammonium hexafluorophosphate) 0.1 M in DCM, working electrode: glassy carbon (3 mm), reference electrode: non-aqueous Ag/Ag$^+$, counter electrode: Pt (2 mm), potential window: -2.0 V – 2.0 V with a scan rate of 0.08 V s^{-1}.

High thermal stability is also a desired characteristic of these lithium salts used in LIBs.[12] The thermal decomposition of the lithium salt **Li[B(DPN)$_2$]** was examined by TGA (Thermal Gravimetric Analysis) and the results are presented in Figure 4. **Li[B(DPN)$_2$]** is stable at temperatures below 240 °C which is when the salt starts to decompose. This temperature value is well above the standard operating temperatures of a LIB which operates between 20–40 °C.[12,47,48] After decomposition ends, roughly 28% of the material remains as a solid. The retention of some material after decomposition is worth noting given that this is not the case for commercially used Li salts.[7] This suggest that by adding phosphate moieties and chelating the molecule to a borate; the material may gain some thermal tolerance.

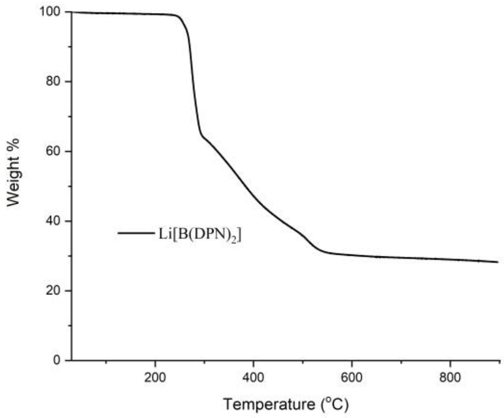


Figure 4. TGA of **Li[B(DPN)$_2$]**.

In previous work, we showed that the mixed boron anion **Li[B(DPC)(ox)]** and phosphorus centered anion **Li[P(DPC)$_3$]** salts could be easily prepared.[29] We have found that the DPN group offers access to corresponding DPN analogues using protocols developed for the DPC compounds. Reaction of **H$_2$-DPN**, oxalic acid and boric acid (Scheme 2, middle) afforded the desired salt **Li[B(DPN)(ox)]** after workup and drying as a white solid in 50% yield. This yield reduced due to the fact that some of the homoleptic salts were also formed during the synthesis. Despite extensive drying, the isolated material retains a molecule of water, possibly indicating coordination of water to the lithium cation. The ^{31}P{H} spectra for this heteroleptic compound presents a resonance at δ = -14.8 ppm. This is a notable upfield shift from δ = 15.6 ppm that is observed in the **Li[B(DPN)$_2$]** salt. The ^{11}B spectra for **Li[B(DPN)(ox)]** displays a resonance at δ = 10.9 ppm, also representing an upfield shift from **Li[B(DPN)$_2$]** which has a resonance at δ = 14.3 ppm.

The synthesis of the phosphorus centered DPN lithium salt **Li[P(DPN)$_3$]** begins by reaction of **H$_2$-DPN** with phosphorus pentachloride, which produced the intermediary H[P(DPN)$_3$] in 93% crude yield as a brown solid (Scheme 2, lower). Addition of lithium *tert*-butoxide exchanges the proton for lithium, and after workup **Li[P(DPN)$_3$]** was obtained as a highly hygroscopic white powder in 73% yield. The ^{31}P{H} spectra for this compound presents two resonances at δ = 10.8 and δ = -89.6

ppm. These two resonances, in a ratio of 3 to 1 represent the signals for the peripheral phosphate phosphorus atoms and the central heptacoordinated phosphorus atom, respectively. The shifts of these signals compare favourably with the corresponding pair of shifts observed for the DPC analogue **Li[P(DPC)$_3$]** (δ = 10.7, -85.7 ppm), thus confirming the identity of the compound. While unfunctionalized lithium salts of the form Li[B(nat)(ox)] or Li[P(nat)$_3$] appear to be unpublished, the related salt [HNEt$_3$][P(nat)$_3$] has been reported.[49]

Solubility of electrolyte salts is another vital property for retaining a high-capacity battery.[36,50-52] Unfortunately, the naphthalene-based borate salts show limited solubility in standard electrolytic solvents.[42] Typical Li ion salt loading in a battery system is approximately 1M in an organic carbonate.[1,36] Unfortunately, Li[P(DPN)$_3$] is nearly insoluble (<0.01M) in an ethylene carbonate (EC) and an ethyl methyl carbonate (EMC) mixture. Li[B(DPN)$_2$] and Li[B(DPN)(ox)], however, showed somewhat better solubility in this solvent mixture (ca 0.04-0.06M). While these latter two complexes showed improved solubility over the previously reported undecorated Li[B(nat)$_2$], their solubility is still lower than previously reported Li[B(DPC)$_2$] (ca 0.1M).[29]

Experimental

Materials:

All reactions were carried out under inert atmosphere using standard Schlenk line techniques. Unless stated otherwise all starting materials and solvents were commercially available and used without further purification. Diethyl ether, tetrahydrofuran, toluene, and benzene were purified by solvent purification system MB-SPS/16-229. Phosphorus pentachloride was sublimed at 179 °C under vacuum. ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra, were recorded using a 400 MHz Varian Inova NMR spectrometer tuned to 399.7, 161.9 and 99.9 MHz respectively, or a 500 MHz Brüker BioSpin NMR spectrometer tuned to 500.24, 126.0 and 202.6 MHz respectively. ^{11}B{H} NMR spectra were obtained on a 300 MHz Varian Mercury NMR spectrometer tuned to 96 MHz or a 500 MHz Bruker BioSpin NMR spectrometer tuned to 160.4 MHz. ^{31}P NMR data obtained from the 400 MHz Varian Inova spectrometer were externally referenced to H_3PO_4. ^{11}B{H} NMR data obtained from the 300 MHz Varian Mercury NMR spectrometer were externally referenced to $BF_3{\cdot}Et_2O$. IR data was obtained using a JASCO FT/IR-4600typeA spectrometer with a diamond ATR. Cyclic voltammograms were measured on a CH Instruments potentiostat 600 series. TGA experiments were performed on a Perkin Elmer DSC 7 using a platinum pan with a N_2 flow rate of 40.0 mL/min. The oven temperature was increased from room temperature to 900 °C with a continuous ramp of 20.00 °C/min. Melting points were measured using a capillary Mel-temp apparatus. Elemental analysis was performed by Robertson Microlit Laboratories, Madison, New Jersey.

Synthesis of (2,3-naphthelene(tetraethyl)bisphosphate):

A 500 mL round bottom flask was flame dried and charged with dry THF (300 mL). Dihydroxynaphthalene (10.00 g, 62.43 mmol) was dissolved in the flask under positive pressure and the solution was cooled to -78 °C, and stirred for 30 minutes. Under positive pressure of nitrogen, diethyl chlorophosphite (18.1 mL, 125 mmol) and triethyl amine (17.4 mL, 125 mmol) were added via syringe and the solution was stirred overnight. A white precipitate was removed from the solution by filtered through a bed of celite. The volatiles were removed from the filtrate under reduced pressure, leaving a light brown oil. The oil was dissolved in diethyl ether (150 mL) and washed with an aqueous solution of 1M sodium hydroxide (3 X 150 mL). The organic layer was dried over sodium sulfate and the solvent was removed under reduced pressure yielding 2,3-naphthelene(tetraethyl)bisphosphate as a yellow oil (12.23 g, 46.8%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.77 (t, *J* = 8.4 Hz, 1H), 7.70 – 7.62 (m, 1H), 7.34 (dt, *J* = 14.6, 3.8 Hz, 1H), 4.30 – 4.08 (m, 4H), 1.26 (dt, *J* = 14.2, 7.2 Hz, 6H). ^{31}P NMR (202 MHz, Chloroform-*d*) δ -6.5.

Synthesis of H_2-DPN (tetraethyl (2,3-dihydroxy-1,4-naphthylene)bis(phosphonate)):

A 250 mL 2-neck round bottom flask was flame dried and charged with dry THF (200 mL) and placed under inert atmosphere. An addition funnel was affixed to the flask and the solution was cooled to -78 °C with stirring for 10 minutes. Diisopropylamine (6.98 mL, 49.7 mmol) was added via syringe, followed by a dropwise addition of ***n***-BuLi (18.2 mL, 49.7 mmol). After stirring for 1 hour the solution turned light yellow. A solution of 2,3-naphthelene(tetraethyl)bisphosphate (3.58 g, 8.28 mmol) in THF (40 mL) was added via syringe to the reaction dropwise and stirred for an hour. The reaction was warmed to RT, and stirred for 2 hrs during which time the solution turned brick red. The reaction was quenched with dilute HCl (1 M, 100 mL). The mixture was then extracted with diethylether (100 mL X 3), washed with brine, dried over with $MgSO_4$, filtered, and concentrated to yield a light brown solid. The solid was the recrystalized by slow evaporation in warm ethanol to provide **H_2-DPN** as white crystals (2.73 g, 76.2%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 12.31 (d, *J* = 1.5 Hz, 1H), 8.05 (ddd, *J* = 6.6, 3.5, 1.8 Hz, 1H), 7.39 (dd, *J* = 6.4, 3.3 Hz, 1H), 4.31 – 4.16 (m, 2H), 4.11 – 3.95 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 6H).^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.86 (dd, *J* = 19.1, 6.7 Hz), 127.45 – 126.17 (m), 125.52 – 124.28 (m), 105.07, 62.99 (d, *J* = 4.2 Hz), 16.82 – 15.20 (m). ^{31}P NMR (202 MHz, Chloroform-*d*) δ 25.4 – 21.7 (m). Anal. Calc. for $C_{36}H_{48}BO_{16}P_4$ C, 49.62; H, 5.55; P, 14.22. Found: C, 49.90; H, 6.11; P, 14.40.

Synthesis of Li[B(DPN)$_2$] (lithium octaethyl ($2\lambda^4$-2,2'-spirobi[naphtho[2,3-*d*][1,3,2]dioxaborole]-4,4',9,9'-tetrayl)tetrakis(phosphonate)):

In a flame dried 100 mL round bottom flask, **H_2-DPN** (1.02 g, 2.35 mmol) and $B(OH)_3$ (0.10 g, 1.4 mmol) were dissolved in toluene (35 mL). The solution was stirred for 10 minutes and LiO*t*-Bu (0.10 g, 1.2 mmol) was added to the flask. To the round bottom flask, a Dean Stark trap was affixed, and the reaction was refluxed for 24 hrs at 120 °C. The reaction was cooled to RT during which an off-white precipitate formed. The off-white solid was collected via vacuum filtration and dried yielding a white solid. The solid was recrystallized by dissolving in methanol and layering with ethyl acetate providing colorless crystals (0.795 g, 76.9%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.64 (ddd, *J* = 6.7, 3.4, 1.6 Hz, 4H), 7.33 (dd, *J* = 6.5, 3.5 Hz, 4H), 4.08 – 3.98 (m, 16H), 1.18 (t, *J* = 7.1 Hz, 24H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 156.27, 129.32, 126.50, 124.22, 103.64 (d, *J* = 181.3 Hz), 62.07, 16.71. ^{31}P NMR (202 MHz, DMSO-d_6) δ 15.6 (t, *J* = 8.3 Hz). ^{11}B NMR (160 MHz, DMSO-d_6) δ 14.35. (IR, λ, cm^{-1}): 2979, 1382, 1010, 958, 600.

Synthesis of Li[B(DPN)(Oxalato)] ·H_2O (tetraethyl (4',5'-dioxo-2l4-spiro[naphtho[2,3-d][1,3,2]dioxaborole-2,2'-[1,3,2]dioxaborolane]-4,9-diyl)bis(phosphonate)):

To a flame dried 100 mL round bottom flask **H_2-DPN** (0.171 g, 0.398 mmol) and oxalic acid (0.036 g, 0.40 mmol) were dissolved in toluene (20 mL). A condenser was affixed to the flask and the reaction was placed in a sand bath and set to reflux, generating a white slurry. A solution of boric acid (0.025 g, 0.40 mmol) and lithium *t*-butoxide (0.031 g, 0.39 mmol) in toluene (10 mL) was added and a Dean-Stark trap was affixed to the flask. The reaction was stirred for 22 hours and was removed from the heat. The reaction was chilled to 0 °C during which an off-white precipitate formed and the reaction was filtered. An off-white solid was collected and washed three times with cold diethyl ether, yielding a white solid. The residual ether was removed under vacuum yielding **Li[B(DPN)(ox)] ·H_2O** as a white solid (0.105 g, 50.5%).

Mp > 300 °C. ^{1}H NMR (500.2 MHz, DMSO-d_6) δ 8.57 (m, 2H), 7.36 (m, 2H), 4.04 (m, 8H), 1.21 (t, J = 7.0 Hz); ^{13}C{^{1}H} NMR δ 159.2, 155.1 (m), 128.73 (t, J_{PC} = 11 Hz), 126.2, 124.4, 104.7 (d, J_{PC} = 182Hz), 62.0 (m), 16.3 (m) ; ^{11}B{^{1}H} NMR (160.5 MHz, DMSO-d_6) δ 10.9 ^{31}P{^{1}H} NMR (202.52 MHz, DMSO-d_6) δ -14.8. Anal. Calcd. for $C_{20}H_{26}O_{13}LiBP_2$: C, 43.35; H, 4.73. Found C, 43.92; H 4.30.

Synthesis of H[P(DPN)$_3$]:

To a 100 mL flame dried, round bottom-flask phosphorus pentachloride (0.111 g, 0.533 mmol) and toluene (20 mL) were added. Once all solid had dissolved, a solution of **H_2-DPN** (0.714 g, 1.65 mmol) in toluene (10 mL) was added dropwise via cannula. The reaction was monitored by determining the pH of an external water bath attached to the nitrogen gas outlet. After 16 hrs, the pH of the bath no longer changed. The solution was concentrated under vacuum yielding a hygroscopic brown gel. The brown gel was washed repeatedly with diethyl ether, yielding mildly air sensitive intermediate species H[P(DPN)$_3$] as a brown solid. (0.283g, 93%).

^{1}H NMR (399.7 MHz, DMSO-d_6) δ 0.69 (t, $^{3}J_{HH}$ = 8.0Hz), 1.21 (m), 3.68 (m), 4.12 (m), 7.16 (m), 7.24 (m), 7.37 (m), 7.46 (m), 7.99 (broad) 8.75 (m) 12.21(broad); ^{31}P{^{1}H} NMR (162.0 MHz, DMSO-d_6) δ -85.4, 14.9, 24.4.

Synthesis of Li[P(DPN)$_3$]:

To a dry, 50 mL round-bottom flask containing lithium *tert*-butoxide (0.408 g, 0.510 mmol), a solution of H[P(DPN)$_3$] (0.283g, 0.496 mmol) in THF (10 mL) was added via syringe. The reaction was stirred for 16 hrs, precipitating an off-white solid. The mother liquor was decanted off, and the solid was thrice washed with diethyl ether, yielding a white solid. The solid was dried under vacuum to yield **Li[P(DPN)$_3$]** as a white powder 0.511 g, 73%.

Mp = 177-179 °C; ^{1}H NMR (399.8 MHz, DMSO-d_6) δ 8.75 (m, 6H), 7.38 (m, 6H), 4.00-4.19 (m, 12H), 3.58-3.77 (m, 12H), 1.21 (t, 7 Hz, 18H), 0.68 (t, 7 Hz, 18H); ^{31}P{^{1}H} NMR (162.0 MHz, DMSO-d_6) δ 10.8, -89.6. Anal. Calcd. for $C_{54}H_{72}O_{24}P_7Li$: C, 48.81; H, 5.46. Found: C, 48.45; H, 5.46.

Conclusions

In summary, a π-extended chelating ligand and a π-extended FRION salt have been prepared and characterized. The crystal structure of the chelating ligand (**H_2-DPN**) showed there is intramolecular hydrogen bonding between phosphoryl oxygens and hydroxyl hydrogens. Furthermore, an X-ray crystallographic study of **Li[B(DPN)$_2$]** not only confirmed the molecular structure but also gave insight on how this salt aggregates in the solid state due to lithium cations coordinating between **[B(DPN)$_2$]$^-$** anions. Electrochemical studies suggest that an addition of electron withdrawing groups and extending the π-system expands the electrochemical window of these molecules, ensuring they are electrochemically stable within the working components of the battery. The salts showed good thermal stability.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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