Boron Chemistry Lights the Way: Optical Properties of Molecular and Polymeric Systems**

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Electrooptical and electronic materials are the subject of much research interest, whereby the focus has often been on electron-rich organic molecules. In the past years, new routes to electron-deficient systems have been developed that take advantage of the fact that three-coordinate boron is isoelectronic and isostructural with a positively charged carbocation, which allows neutral, p-type materials to be synthesized directly. This minireview summarizes recent work on compounds with 3- and 4-coordinate boron as well as boron clusters, placing it in the context of prior studies by the research groups of Williams and Glowgowski, Kaim, Lequan, and Marder.

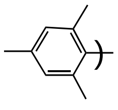
1. Introduction

Nonlinear optical (NLO) and electrooptical (EO) properties of polymeric and molecular materials have been the subject of an explosion of interest in the past decade, with the increasing realization that traditional inorganic solid-state materials can be replaced by organic and organo-element materials which are easier and cheaper to fabricate.[1, 2] In the search for new materials, the properties of a diverse array of boron-containing systems have been investigated, from NLO chromophores to the emitting or electron-transporting components in multilayer organic light-emitting diodes (OLEDs).

Research into new EO and electronic materials has concentrated on electron-rich organic molecules often containing nitrogen, sulfur, or selenium. Electron-deficient systems are usually arrived at by oxidative doping. As three-coordinate boron is isoelectronic and isostructural with a positively charged carbocation, an alternative strategy is to replace carbon atoms with boron, allowing neutral, p-type materials to be synthesized directly. It should be noted that three-coordinate nitrogen is isoelectronic with a carbanion, in effect the mirror image of boron in this respect. Whilst there has been a huge amount of research aimed at exploiting this property of nitrogen to produce n-type materials, for example for hole transporters in OLEDs[3] and for two-photon absorption,[4] research into the analogous boron-substituted materials has been surprisingly limited. In part, this may be due to the relative lack of stability, particularly to hydrolysis, of many boron systems when compared to C- or N-based compounds. In recent years, however, a large number of boron-containing compounds which exhibit enhanced stability to moisture and oxygen have been synthesized, allowing the development of new materials with second- and third-order NLO properties. They are also under investigation for photoluminescence (PL) and electroluminescence (EL) applications, with a particular focus on the generation of blue EL for OLEDs.

2. Three-Coordinate Boron

With its vacant p_z orbital, three-coordinate boron is inherently electron deficient and is a strong π-electron acceptor. In contrast to other strong π acceptors such as the nitro group, however, three-coordinate boron is not generally inductively electron withdrawing and may well be a σ donor. The vacant p_z orbital also allows for conjugation of organic π systems with and through boron, and it has been shown that significant delocalization occurs. Kinetic stability towards air and moisture can be achieved by steric hindrance of the p_z orbital by bulky substituents. In particular, the mesityl (2,4,6-trimethylphenyl, Mes, **1**) group has been used to synthesize a great number of air-stable organoboranes.



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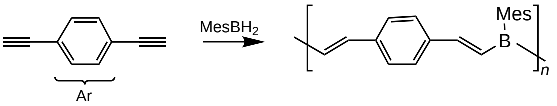
Recently, several π-conjugated polymers containing boron in the polymer chain have been synthesized by Chujo et al.[5] The hydroboration of aromatic and heteroaromatic diynes with mesitylborane [Eq. (1)][6] was employed to synthesize



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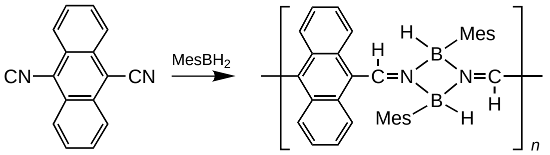
polymers of the general form shown in Equation 1 that are related to poly-*p*-phenylene vinylene (PPV), but contain boron conjugated in the main chain. Despite having relatively low molecular weights, these polymers exhibited strong PL in the blue region. With heteroaromatic diynes, the resulting polymers displayed much larger Stokes shifts resulting in green (Ar = furandiyl, thiophenediyl) or white emission (Ar = pyridinediyl). The polymer based on diethynylbenzene also displayed an unusually large third-order nonlinear optical susceptibility ($\chi^{(3)}$) of 6.87×10^{-6} esu, more than a thousand times higher than that of all-*trans*-polyacetylene as measured by degenerate four-wave mixing.[5]

A different strategy, the polycondensation of difunctional Grignard reagents with aryldimethoxyboranes, was used to produce poly(*p*-phenyleneborane)s.[7] All such polymers were found to be highly fluorescent in the 477–496 nm region, with sterically demanding mesityl or tripyl (2,4,6-$i\mathrm{Pr}_3\mathrm{C}_6\mathrm{H}_2$) groups on boron providing stability. Hydroboration polymerization of dicyano compounds with mesitylborane provided another class of polymers, poly(cyclodiborazane)s.[8] For example, hydroboration polymerization of 9,10-dicyanoanthracene [Eq. (2)] produced a polymer having a broad emission in the green region (494 nm). Polymers containing both boron and the transition metals ruthenium, palladium, or platinum in the main chain have also been prepared.[9] The absorption and fluorescence spectra of these polymers indicate a high degree of π delocalization via boron and the metal atoms. The interaction between metal and boron was highly dependent on the nature of the metal involved. Boration copolymerization of silanes and aromatic diynes[10] or dinitriles[8c] was used to prepare novel σ-π conjugated polymers which proved to be highly fluorescent.



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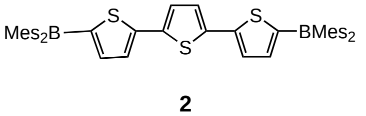
Shirota et al. have investigated the properties of oligothiophenes of the form $(\mathrm{Mes})_2\mathrm{B}(\mathrm{X})_n\mathrm{B}(\mathrm{Mes})_2$ where X = 2,5-thiophenediyl and $n = 2$ (BMB-2T) or 3 (BMB-3T, **2**).[11] These compounds readily formed amorphous glasses with relatively high glass transition temperatures (T_g), and were found to have good electron-transporting properties. BMB-2T was also found to electroluminesce with $\lambda_{\max} = 446$ and 472 nm. These properties were utilized in the construction of multilayer OLEDs. Both BMB-2T and BMB-3T were incorporated as the electron-transporting layer in a green OLED with Alq_3 (q = 8-hydroxyquinolato, **10**) as the emitting layer; BMB-2T was also used as the emitting layer to construct a blue OLED. This device exhibited a maximum luminance of 1700 cd m^{-2} at a driving voltage of 17 V, comparing favorably with blue OLEDs using oxadiazole- or triazole-based materials, which typically display a maximum luminance of ca. 1000 cd m^{-2}.[12] The related compounds 1,3-bis(5-(dimesitylboryl)thiophen-2-yl)benzene and 1,3,5-tris[5-(dimesitylboryl)thiophen-2-yl]benzene have also been investigated, and were found to be effective electron transporters and hole blockers.[13] The asymmetric compounds $\mathrm{Ar_2NXB(Mes)_2}$ where X = (1,4-phenylene)thienyl and Ar = 4-methylphenyl (**3**) or 2-(9,9-dimethylfluorenyl) have also been shown to exhibit strong EL behavior.[14] A recent extension of this work has seen the triarylamine tris{4-[5-(dimesitylboryl)thiophen-2-yl]phenyl}-amine incorporated into photovoltaic devices.[15]



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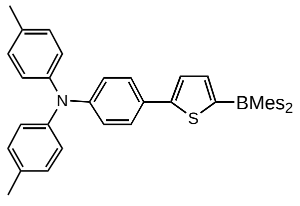

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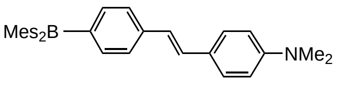
Lequan et al. have investigated the NLO properties of donor–acceptor (D-A) substituted oligothiophenes, once again using $\mathrm{B(Mes)_2}$ groups as the acceptor moiety.[16] First molecular hyperpolarizabilities (β) were measured by EFISH (electric field induced second harmonic generation), and were found to be significantly larger than for biphenyl-based systems. This was attributed to two factors: the reduced aromaticity of thiophene compared with benzene, thus increasing the delocalization of electrons from donor to acceptor; and the greater planarity of oligothiophenes due to the reduction of steric hindrance.

Polythiophenes containing 3-coordinate boron have been prepared by Corriu and Siebert et al.[17] These polymers were intensely colored and displayed a marked bathochromic shift in absorption compared to the corresponding monomers, indicating conjugation of the π system through boron. However, the polymers had limited stability due to the lack of bulky substituents to prevent access to the vacant p_z orbital of boron.

Molecules and oligomers based on rigid, π-conjugated rods have attracted much attention for their NLO properties,[18] with much of the research concerning delocalized D-A systems. These exhibit a large change in dipole moment upon excitation, a characteristic that gives rise to a large value of β.

The dimesitylboryl group has also been used as the electron-accepting moiety in molecules of the form $\mathrm{DXB(Mes)_2}$. Marder et al. have prepared a wide range of such molecules and investigated their second-order and third-order NLO properties;[18] donors D included MeO, MeS, $\mathrm{H_2N}$, $\mathrm{Me_2N}$, $\mathrm{Ph_2P}$, ferrocenyl moieties, and various conjugated alkene, alkyne, aryl or mixed π systems. In addition, they have investigated symmetric bis[$\mathrm{B(Mes)_2}$] compounds.[19] Hydroboration of terminal alkynes was used to prepare molecules with vinyl-$\mathrm{B(Mes)_2}$ groups, whereas aryl and alkynyl derivatives were prepared by lithiation followed by reaction with $\mathrm{FB(Mes)_2}$. Although these compounds had unusually small ground state dipole moments, their β values, measured by EFISH, were in the range of those of the cyano or nitro acceptor analogues. For example, $\beta_{1.907\,\mu m}$ for compound **4** is 45×10^{-30} esu. The third-order NLO properties of bis[B(Mes)$_2$] compounds were investigated by third harmonic generation (THG), and it was found that the B(Mes)$_2$ group was superior to the nitro group for increasing γ values. Well characterized compounds such as **5** represent models for the polymers synthesized more recently.[5, 6]



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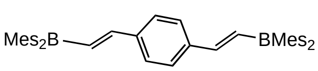

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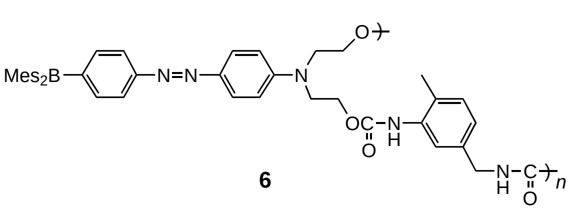
In addition, Lequan et al. have investigated the second-order NLO properties of rods where D = dimethylamino and X = biphenyldiyl (BNB) or $C_6H_4N{=}NC_6H_4$ (BNA),[20, 21] which gave β values (EFISH) of 32×10^{-30} and 47×10^{-30} esu and UV/Vis absorption maxima of 376 and 446 nm, respectively. The greater electron delocalization in the azo compound was suggested as the cause of the differences between these compounds. A modified version of BNA was later incorporated as a side chain in polyurethane-based polymers (**6**),[22] which were poled under an external electric field using the corona technique,[23] and the second harmonic of the resulting thin films examined. The magnitude of the second harmonic generation (SHG) signal was found to be strongly dependent upon the poling time, but relatively large quadratic susceptibilities were observed for these materials.



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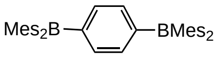
The electron-accepting properties of the B(Mes)$_2$ group were investigated by Kaim et al. in an electrochemical study of *p*-phenylenediboranes.[24] These compounds were found to exhibit redox properties that were opposite in nature but similar in magnitude to the analogous *p*-phenylenediamines, with 1,4-bis(dimesitylboryl)benzene (**7**) having two reversible electrochemical reduction steps leading to the radical anion and the dianion. This work suggested that B(Mes)$_2$ should prove useful in D-A compounds, with ENDOR spectroscopy suggesting that considerable delocalization of the unpaired electron occurs in the radical. Further investigation of the electronic properties of arylboranes by cyclic voltammetry and UV/Vis spectroscopy[25] showed that a single mesityl group was sufficient to provide stabilization of the singly reduced radical anion.



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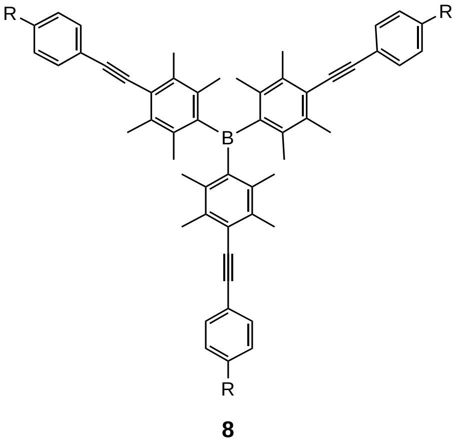
UV/Vis/near-IR spectroelectrochemistry was used to investigate the compounds **7**, 4,4′-bis(dimesitylboryl)biphenyl, and PhB(Mes)$_2$.[26] The radical anions and dianions were all found to absorb strongly in the visible or near-IR region,[18c, 27] with absorption bands of the radical anions resembling those of the analogous isoelectronic amine radical cations. Ab initio[27] and density functional[18a] calculations on BH$_2$-substituted analogues of these compounds demonstrated a quinoidal distortion of the organoboron systems upon reduction, suggesting conjugation of the boron p orbital with the organic π system. These calculations supported earlier EPR/ENDOR measurements on the radicals,[27] thereby providing further evidence of their electronic structure.

Photochemical studies of dimesitylphenylboranes were first conducted by Williams et al.[28] Investigation of the fluorescence quantum yields for various *para*-substituted compounds showed an increase in the quantum yield with electron-donating substituents and a marked solvatochromic dependence on the position of the fluorescence (but not absorption) maxima. This result indicated stabilization of a charge transfer excited state species having a large dipole moment by increasingly polar solvents, which could only be possible if the boron atom was capable of conjugation with the phenyl group (see also ref. [18a]). The B(Mes)$_2$ group was later compared to the nitro group in azo dyes.[29] This work suggested that B(Mes)$_2$ was a powerful electron-withdrawing group, comparable in magnitude to the nitro group. From subsequent studies, however, it followed that B(Mes)$_2$ is in fact closer to the cyano group in its electron-withdrawing properties.[25] The photophysics of some related *ortho*-substituted PhB(Mes)$_2$ derivatives has recently been investigated.[30]

Tri(9-anthryl)borane has recently been prepared by Tamao et al.[31] The anthryl group is similar to the mesityl group in that it provides kinetic stability to boron, and UV/Vis and theoretical studies demonstrated that π conjugation is extended throughout the entire molecule. Using B(Mes)$_2$-substituted derivatives of anthracene, starburst oligomers with multiple boron centers were prepared. Complexation of fluoride anions at boron disrupts π conjugation in these molecules, allowing them to behave as fluoride-selective chemosensors.[32] This group has also prepared substituted tridurylboranes (**8**), which display interesting photophysical properties. Such systems offer a new approach to the



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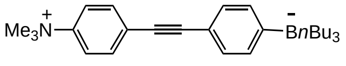
construction of electron-deficient materials, which could potentially be used in organic electronic devices.[33]

Rigid rods containing anionic boratastilbene and (boratastyryl)stilbene units have been prepared by hydrozirconation using $[\mathrm{Cp_2Zr(H)Cl}]$ with an appropriate alkyne followed by transmetalation and reduction with sodium hydride.[34] The photophysics of these compounds was found to be dependent upon solvent effects, suggested to be due to aggregation and conjugation length.

3. Four-Coordinate Boron

Zwitterionic borates **9** with conjugated π systems show interesting second-order NLO properties.[35] Compared to analogous, uncharged D-A molecules, they are of higher transparency and have much higher $\mu\beta_0$ values due to their increased dipole moments. For example, $\mathrm{Me_3\overset{+}{N}C_6H_4CH{=}CHCH{=}CHC_6H_4\bar{B}Bu_3}$ was found to have a $\mu\beta_0$ value of approximately 3250×10^{-48} esu. The large dipole moments should favor the alignment of these molecules in polymer films, thus enhancing macroscopic NLO properties. Upon excitation, these zwitterionic compounds experience a dipole change in the opposite sense to uncharged D-A molecules, with the excited state having a lower dipole moment than the ground state.



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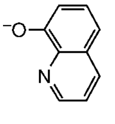
The investigation of the second-order NLO properties of borane adducts of stilbazoles and pyridines revealed[36] that they exhibit significantly higher β values than the corresponding (uncomplexed) stilbazoles or pyridines, and values of μβ were also much enhanced. Recently, a theoretical study of this system has produced results in good agreement with the experimental data.[37]

Efficient green EL from a thin film of $\mathrm{Alq_3}$ (q = 8-hydroxyquinolato, **10**) was first reported by Tang and van Slyke in 1987,[38] and $\mathrm{Alq_3}$ has since been used extensively as the electron-transporting and emissive layers in OLEDs. Whilst OLEDs emitting in the green and red regions of the spectrum have been developed by doping $\mathrm{Alq_3}$ with various dyes, the blue region has proved harder to attain by this method. In recent years, however, a number of 4-coordinate boron systems have been observed to emit in the blue region.



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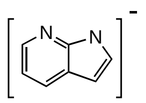
There have been a number of studies on boron analogues of $\mathrm{Alq_3}$. Whilst $\mathrm{Alq_3}$ is octahedral, with bidentate ligands, the smaller size of boron prevents this. Compounds of the form $\mathrm{BR_2q}$ are tetrahedral, with a bidentate quinolato ligand,[39] but $\mathrm{Bq_4^-}$ anions have monodentate coordination through oxygen.[40] Generally, the boron compounds emit at shorter wavelengths and are more covalent in nature than their Al relatives, leading to greater stability towards air and water. The quantum efficiency of emission is higher than that of $\mathrm{Alq_3}$ derivatives, and some of the compounds have also been found to have excellent electron-transporting properties.

Strong blue EL has been observed for the air-stable diborates $\mathrm{B_2(\mu\text{-}O)Et_2(azain)_2}$ and $\mathrm{B_2(\mu\text{-}O)Ph_2(azain)_2}$ (azain = 7-azaindole anion, **11**)[41] and for the complexes $\mathrm{BPh_2(2\text{-}py\text{-}in)}$ and $\mathrm{BPh_2(2\text{-}py\text{-}aza)}$ (2-py-in = 2-(2-pyridyl)indole, 2-py-aza = 2-(2-pyridyl)-7-azaindole).[42] A boron compound with one pyridinium and two phenolate units, (dppy)BF (**12**), has also been used to construct EL devices with strong emission at either 550 or 450 nm, though it is uncertain whether **2** functions as the electron-transporting or emissive material.[43] A particularly versatile chromophore is offered by boron–dipyrrin compounds **13**. These fluorescent dyes have been investigated for a variety of purposes from light-harvesting arrays to doping $\mathrm{Alq_3}$ OLEDs.[44]



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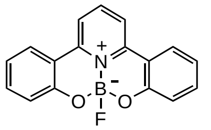

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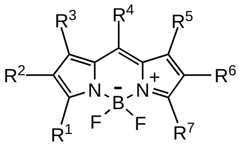

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4. Borane and Carborane Clusters

A number of boron cluster compounds have been investigated for their NLO properties. The molecular hyperpolarizibilities of a series of disubstituted carboranes have been studied by SHG and EFISH,[45] but were found to be generally low. Recently, however, with the carborane ylide $12\text{-}\mathrm{C_7H_6^+{-}CB_{11}H_{11}^-}$ a compound has been synthesized that displays a β value of $(236 \pm 50) \times 10^{-30}$ esu by HRS (HRS = hyper Rayleigh scattering)[46] and was also found to be transparent below 400 nm.

Theoretical work has also suggested the potential of boranes and carboranes for second-order NLO. The structures and second-order responses for *nido*-, *conjuncto*-, and *closo*-boranes bearing tropylium and cyclopentadienyl substituents have been calculated using semiempirical methods (MOPAC AM1), as have those of the corresponding *ortho*-, *meta*-, and *para*-carboranes.[47] Some of these clusters were predicted to exhibit surprisingly large β and μβ values. For example, $[\mathrm{(C_7H_6)C_2B_{10}H_{10}(C_5Me_4)}]$ was calculated to have $\beta = 682 \times 10^{-30}$ and $\mu\beta = 12\,000 \times 10^{-48}$ esu. Ab initio molecular orbital calculations have also suggested that dimeric carborane anions should display NLO properties.[48]

A recent study of some novel carborane–fullerene dyads[49] revealed unexpectedly large β values of up to 1189×10^{-30} esu for these materials; no explanation of these properties is available at present. The potential use of carboranes in optoelectronics has received very little attention. The hafnium–carborane complex $[\mathrm{Hf}(\eta^5{:}\eta^1\text{-}(\mathrm{C_5H_4CMe_2)CB_{10}H_{10}C})_2]$ displays both EL and mechanoluminescence.[50]

In summary, molecular and polymeric boron-containing compounds exhibit a wide variety of useful optical properties. It is clear that some of these compounds have great potential in the fields of linear and nonlinear optics, which should stimulate research on these systems.

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