Abstract: Organoboron compounds are attracting immense research interest due to their wide range of applications. Particularly, low-coordinate organoboron complexes are receiving more attention due to their improbable optical and nonlinear optical properties, which makes them better candidates for medical applications. In this review, we summarize the various synthetic methods including multicomponent reactions, microwave-assisted and traditional pathways of organoboron complexes, and their optical and nonlinear properties. This review also includes the usage of organoboron complexes in various fields including biomedical applications.

Keywords: organoboron; synthesis fluorescence; nonlinear optical; imaging

1. N-B-N Environment in Organoboron Compounds

The chemistry of organoboron compounds is one of the most multifaceted research areas among heteroatom-substituted organic molecules. These organoboron compounds have vast applications in numerous fields including biomedical and nuclear chemistry [1–4]. There is a dramatic rise in the research on the applications of boronic acid and their derivatives [5–9]. Boron is an interesting molecule with an electron-deficient character and is also more electropositive than carbon. This rudimentary property of boron has been completely utilized in synthesizing various organoboron compounds and exploring their applications in organic synthesis [10–15].

The report by Treibs and Kreuzer on BODIPY derivatives have opened up an exciting and useful field in chemistry. Since then, BODIPY chemistry has grown immensely and reports have poured in for the different ways of synthesis of BODIPY compounds and their applications. These applications include their uses in laser dyes, protein tags, and metal sensors. Fluorescent compounds have seen the limelight as these are most importantly studied by various research communities in multidisciplinary areas. Among all the other fluorescent compounds, boron-containing compounds are of utmost interest these days as they have significant and thrilling applications in various fields as active media of tunable lasers; development of photoelectronic devices, fluorescent probes, and chemical sensors; or monitoring the physicochemical characteristics of the surrounding ambiances. They also have optical features, as these compounds show better photo-stability, robust fluorescence intensity, high quantum yields, and small Stokes shift [16]. Even though these systems are known for intrinsic potential applications, their photophysical properties are highly focused so as to design new dyes with specific properties. This can be performed by changing the molecular structure of the chromophore (substituent effect) and the environmental conditions (solvent effect, incorporation in rigid solid materials, etc.) [17].
In this review, we summarize the various synthetic methods including multicomponent reactions, microwave-assisted and traditional pathways of organoboron complexes, and their optical and nonlinear properties. This review also includes the usage of organoboron complexes in various fields including biomedical applications.

2. Organoboron Compounds Having NBN Framework

In recent times, there has been increasingly immense research interest in BODIPY (boron-dipyrromethene) compounds containing distinct substituent groups (with heteroelements in meso and other positions) based on NBN ligand core [18]. This is due to their attractive properties as they are tunable for fluorescence emission in 500–700 nm regions with high fluorescent quantum yield in various solutions and good photostability [19–22]. These fluorescent compounds have found profound applications as tracers in fluorescence microscopy in fluorescence immunoassay and in flow cytometric analysis, along with a series of other useful applications [23–28].

In this review, we summarize a series of new meso-polyarylamine-BODIPY hybrids of the general structure (A) Scheme 1, which were synthesized by two different modified methods.

**Scheme 1.** General synthesis of 8-substituted BODIPYs with the Liebeskind–Srogl cross-coupling.

(A) Liebeskind–Srogl coupling: Cross-coupling of thiomethyl BODIPYs with arylaminoboronic acids [29].

(B) Liebeskind–Srogl and Suzuki coupling: By a two-step sequence, a reaction to prepare meso-bromoaryl BODIPYs followed by coupling of these Bromine-containing BODIPYs with arylaminoboronic acids [30–35].

Several of these derivatives exhibited emission in the near-infrared region. BODIPY derivatives of 2-thienyl and 2,6-bisthiényl displayed intense absorption and a large Stokes shift in contrast with the typical BODIPY.

Based on DFT calculations [36–38], it was proposed that the large Stokes shifts of 3, 4, and 5 (Scheme 2) are due to the remarkable geometry relaxation upon photoexcitation and its substantial effect on the energy levels of molecular orbitals. For the dyes with small Stokes shifts, much smaller geometry relaxations were found [39–41].
The properties of aza-BODIPY compounds (Scheme 3) containing methoxy and hydroxyl groups. The study on linear absorption spectra for phenolate forms of aza-BODIPY containing hydroxyl group exhibited drastic changes and showed new bands for phenolate groups in the region below 500 nm and above 700 nm in THF solutions. In addition, no fluorescence signals were observed with 600 nm excitation for phenolate forms. Moreover, these hydroxyl group (HABDP)-containing azo-BODIPY compounds revealed two photon absorption properties at 1200–1450 nm spectral range [43].

Reports [44] on the properties of aza-BODIPY containing triphenylamine, 4-ethynyl-N,N-dimethylaniline, and methoxy moieties (Scheme 4) such as substitution and charge transfer on linear and nonlinear optical absorption (especially two-photon absorption) were investigated by ultrafast pump–probe spectroscopy technique. It was observed that aza-BODIPY compounds with good electron-donating moieties (triphenylamine and 4-ethynyl-N,N-dimethylaniline moieties) have charge transfer from electron-donating parts of the molecules to aza-BODIPY core. The two-photon absorption cross sections increase with the electron-donating strength.
Additionally, 1,8-naphthyridine–BF$_2$ complexes 15–18 were synthesized (Scheme 5); these are known for their good fluorescence properties. These complexes contain one N atom less between naphthyridine moieties that have strong emissions in the solid state (Figure 1) [45]. Both naphthyridine and pyridine units in their structure are ligated to the BF$_2$ core as monodentate ligands, and the two aromatic units are nearly coplanar with dihedral angles of 4.91 and 2.968 for the B- and N-form crystals, respectively. SEM and TEM images of 17 showed that it consists of tangled nanowires of width about 30 nm and lengths varying from several hundred nanometers to several micrometers (Figure 2).

![Scheme 4. Structures of investigated compounds.](image)

![Scheme 5. Synthetic routes to and chemical structures of 1, 8-naphthyridine derivatives 15–18.](image)
Additionally, 1,8-naphthyridine–BF$_2$ complexes 15–18 were synthesized (Scheme 5); these are known for their good fluorescence properties. These complexes contain one N atom less between naphthyridine moieties that have strong emissions in the solid state (Figure 1) [45]. Both naphthyridine and pyridine units in their structure are ligated to the BF$_2$ core as monodentate ligands, and the two aromatic units are nearly coplanar with dihedral angles of 4.91 and 2.968 for the B- and N-form crystals, respectively. SEM and TEM images of 17 showed that it consists of tangled nanowires of width about 30 nm and lengths varying from several hundred nanometers to several micrometers (Figure 2).

Further, some research groups reported a new dye, BF$_2$-rigidified anilido-pyridine boron difluoride (Figure 3), which show large Stokes shifts and high photostability [46]. These are air- as well as moisture-stable and do not undergo photodegradation even upon exposure to continuous radiation. This photostability makes the dye more efficient when compared with BODIPY and many other dyes. Their efficacy as probes for biological membranes was demonstrated using a liposome model.

Besides, other aryl and hetaryl moieties in BODIPY compounds are widely reported. Three two-photon active boradiazaindacene derivatives 2,6-di-phenylacetylenyl-1,3,5,7-tetramethyl-8-phenyl-4,4-difluoroboradiazaindacene (Figure 4, 24a), 2,6-di-9-ethyl-9H-carbazole-3-ethynyl-1,3,5,7-tetramethyl-8-phenyl-4,4-difluoroboradiazaindacene (Figure 4, 24b) and 2,6-di-4-N,N-diphenyl-phenylacetylenyl 1,3,5,7-tetramethyl-8-phenyl-4,4-difluoroboradiazaindacene (Figure 4, 24c) in THF solutions were studied by using femto-second laser spectroscopic techniques [47]. The two-photon fluorescence imaging experiment on these compounds exhibit good cell permeability, nontoxicity, and excellent two-photon fluorescence properties. Structurally rigid BODIPY having spirofluorene moieties [48] (Figure 5) were reported that exhibit intense bathochromic fluorescence. These rigid structures give high quantum yield of photoluminescence and decreased nonradiative decay of excited states. DFT calculations indicated that spiro-conjugation leads to delocalization of the π-system of BODIPY derivatives over the fluorene moieties as well as the BODIPY core. Moreover, symmetric BODIPY dyads (Figure 6) have chromophores at the meso-
position through phenylene bridge or direct linkage [49]. In excited state, these molecules will undergo symmetry-breaking through ICT state. Due to differences in degree of rotational freedom, these dyads will show different behavior of the ICT state. Whereas dyad 25 undergoes rapid nonradiative decay to the ground state, the more hindered dyad 26 has a long-lived ICT state with moderate-to-high fluorescence quantum efficiency. The excited state properties of these dyads could prove useful in facilitating charge separation in photovoltaic devices.

Figure 3. BF₂-rigidified anilido-pyridine boron difluoride dye.

Figure 4. Boradiazaindacene derivatives of 24a, 24b, 24c.
Introduction of radiotracers in BODIPY compounds is also known [50]. The rapid nucleophilic $^{18}$F-radiolabeling of a BODIPY dye in aqueous solutions is reported (Figure 7). This radiolabeled dye was found to be stable in vivo and used as a dual modality imaging agent. Besides several applications of BODIPY compounds, we elucidate that the BODIPY-based fluorescent probe 31 can be used for the selective detection (Figure 8) of tyrosinase (a copper-containing enzyme catalyzing the hydroxylation of phenol derivatives, such as tyrosine or tyramine, which is widespread in plants and animal tissues) activity in buffered aqueous solution [51], is suitable for screening potential inhibitors of tyrosinase, as well as for bioimaging intracellular tyrosinase activity in living cells.

![Figure 5. New approach to structurally constrained BODIPY dyes.](image)

![Figure 6. Symmetric BODIPY dyads with chromophores at the meso position.](image)

![Figure 7. Nucleophilic $^{18}$F-radiolabeling of a BODIPY dye.](image)
Some NBN-environment-based organoboron compounds have also been reported with a wide variety of applications. Thus, optically active organoboron aminoquinolate-based coordination polymers bearing the chiral side chain derived from L-alanine were synthesized (Scheme 6) and their optical behavior was studied by UV–Vis and photoluminescence spectroscopies [52]. The hydrogen-bonding in these polymers was found to be stable in solvents such as CHCl$_3$ and DMF studies of circular dichroism (CD). Intramolecular charge transfer was observed due to the fact of solvents polarity. Further, some toxic compounds such as Triphenyl borane were studied (Figure 9). The toxicity of the alternative organotin (Ot) antifoulants TPBP (triphenylborane pyridine; Figure 9: 34) and TPBOA (triphenylborane octadecylamine; Figure 9: 35) and their degradation products on Crassosteagigas and Hemicentrotus pulcherrimus were tested [53]. Silylated-diborylene-3,4,9,10-tetraaminoperylenes (DIBOTAPs, compounds 39–42) were synthesized by treating 4,9-diaminoperylenequinone-3,10-diimine (DPDI, Scheme 7) with BH$_3$-THF, lithiation with $n$-butyllithium, and subsequent addition of the corresponding silyl chloride (Scheme 8) [54]. In all cases, the perylene backbones were found to be not completely planar. The coordination of the nitrogen donor atoms to the Lewis acidic boron atoms stabilizes the tetraaminoperylene core, while the N-silylation appears to suppress aggregation in solution. The latter enables the high luminescence quantum yields. The exchange of all three methyl groups with ethyl (compound 39) or isopropyl (compound 40) substituents resulted in a significant increase in quantum yields with values of 92% and 89%, respectively. The observed fluorescence decay is monoexponential for all dyes with typical lifetimes of 5.5–6.6 ns.

To conclude, 1D boron containing two-photon absorbing fluorophores with two boron-containing central cores (with two boron atoms)—the cyclodiborazane and the pyrazabole moieties—were reported (Scheme 9) [55]. All compounds present a strong two-photon induced fluorescence and have been used in microscopy to visualize cancerous HeLa cells. High boron content should be of great interest to study the mechanism of boron neutron capture therapy by deep imaging in small animals with micrometric resolution by two-photon excited fluorescence.
Scheme 6. Synthesis of organoboron aminoquinolate-based coordination polymers.

Figure 9. TPBP (34) (triphenylboranepyridine) and TPBOA (35) (triphenylboraneoctadecyl).

Scheme 7. Synthesis of 4,9-diaminoperylenequinone-3,10-diimine (DPDI), 1,3,8,10-tetraazaperylene (TAPP), and 3,4,9,10-tetraaminoperylene (TAP).
Scheme 7. Synthesis of 4,9-diaminoperylenequinone-3,10-diimine (DPDI), 1,3,8,10-tetraazaperopyrene (TAPP), and 3,4,9,10-tetraaminoperylene (TAP).

To conclude, 1D boron containing two-photon absorbing fluorophores with two boron-containing central cores (with two boron atoms) — the cyclodiborazane and the pyrazabole moieties — were reported (Scheme 9) [55]. All compounds present a strong two-photon induced fluorescence and have been used in microscopy to visualize cancerous HeLa cells. High boron content should be of great interest to study the mechanism of boron neutron capture therapy by deep imaging in small animals with micrometric resolution by two-photon excited fluorescence.

Scheme 8. Synthesis of silylated-diborylene-3,4,9,10-tetraaminoperylene compounds 39–42 and TMS-DIBOTAP.

Scheme 9. Chemical structures of prepared fluorophores based on cyclodiborazane and pyrazabole central cores.

\[
\text{DPDI} \quad \text{DOBOTAP}
\]

| TMS-DIBOTAP | \( R^1 = R^2 = R^3 = \text{Me} \) |
|-------------|----------------------------------|
| 39          | \( R^1 = R^2 = R^3 = \text{Et} \) |
| 40          | \( R^1 = R^2 = R^3 = \text{Pr} \) |
| 41          | \( R^1 = R^2 = \text{Me}, R^3 = \text{i-Pr} \) |
| 42          | \( R^1 = R^2 = \text{Me}, R^3 = \text{t-Bu} \) |

Molecules 2022, 27, x FOR PEER REVIEW 11 of 31

A predominant number of boron compounds containing O-B-O framework corresponds to β-diketone derivatives, having been extensively studied for their fluorescent properties [56]. Reports on the first difluoroborate diketone compounds that are curcumin derivatized by the NIR fluorescent probe, CRANAD-2 (Scheme 10), for in vivo biological studies and provides a useful type of NIR fluorescent dye for cell, tissue, and in vivo imaging for small animals [57]. Upon interacting with aggregates, CRANAD-2 undergoes a range of changes, which include a 70-fold fluorescence intensity increase, a 90-nm blue shift (from 805 to 715 nm), and a large increase in quantum yield. After intravenous injection of this probe, 19-month-old Tg2576 mice exhibited significantly higher relative signal than that of the control mice over the same period of time (Figure 10) [58].
3. Compounds Containing O-B-O Framework

A predominant number of boron compounds containing O-B-O-moiety corresponds to \( \beta \)-diketone derivatives, having been extensively studied for their fluorescent properties [56]. Reports on the first difluoroborate diketone compounds that are curcumin-derivatized by the NIR fluorescent probe, CRANAD-2 (Scheme 10), for in vivo biological studies and provides a useful type of NIR fluorescent dye for cell, tissue, and in vivo imaging for small animals [57]. Upon interacting with aggregates, CRANAD-2 undergoes a range of changes, which include a 70-fold fluorescence intensity increase, a 90-nm blue shift (from 805 to 715 nm), and a large increase in quantum yield. After intravenous injection of this probe, 19-month-old Tg2576 mice exhibited significantly higher relative signal than that of the control mice over the same period of time (Figure 10) [58].

![Scheme 10](image)

**Scheme 10.** (Top) Structure of curcumin, compound 49 (CRANAD-1), and compound 50 (CRANAD-2); (bottom) synthetic route for CRANAD-2.

![Figure 10](image)

**Figure 10.** Representative images of Tg2576 mice and control littermates at different time points before and after intravenous injection of 5.0 mg/kg CRANAD-2. (A) 19-month-old control mouse; (B) 19-month-old Tg2576 mouse (mice showed similar background fluorescence signal); (C) the relative fluorescence signal \([F(t)/F(0)]\) was significantly higher than that of the control mice, and the decay of fluorescence signal was significantly slower in transgenic mice compared with the control group (*: \( p < 0.005 \), **: \( p < 0.01 \)).

Surprising process-dependent and reversible mechanochromic fluorescence was discovered for the boron dodecane complex (BF\(_2\)dbmOC\(_{12}\)H\(_{25}\)) (Figure 11)—a difluoroboron dibenzoylmethane dye coupled to a lipid chain [39]. A thermally annealed spin-cast film of the lipid dye on glass exhibited blue fluorescence under UV light; however, after shearing or scratching, the mechanically perturbed region turned yellow–green. The blue coloration
could be rapidly recovered by thermal treatment of the film [60]. In order to test the effects of alkyl chain length on solid-state photoluminescence and reversible mechanochromic luminescence (ML) in difluoroboron β-diketone dyes, a series of dyes, BF$_2$dbmOR, with dibenzoylmethane (dbm) ligands and alkoxyl substituents (-OR) were prepared [61], where $R = C_nH_{2n+1}$ and $n = 1, 2, 3, 5, 6, 12, 14, 16, 18$ (Figure 12). Fluorescence spectra and lifetimes were found to be nearly identical for dyes in CH$_2$Cl$_2$ solution; whereas, emission maxima and lifetimes were different among the samples in the solid state as powders, thin films, or spin cast films. The recovery time generally increased with alkyl chain length, ranging from minutes ($n = 3$) to days ($n = 18$). Longer chain analogues ($n = \frac{1}{2}, 6, 12, 14, 16, 18$) did not fully return to the original annealed emissive state even after months on quartz, though the dynamics are substrate-dependent.

![Figure 11. Structure of BF$_2$dbmOC$_{12}$H$_{25}$.](image1)

![Figure 12. Structure of BF$_2$dbmOR.](image2)

The difluoroboron avobenzone complex (BF$_2$AVB) (Figure 13) is commercially available and used as an ingredient in sunscreen products because of its strong absorption of UVA light (320–400 nm) was synthesized via BF$_3$·OEt$_2$ boronation in CH$_2$Cl$_2$ avobenzone [62]. Unlike BF$_2$dbm(s) derivatives that typically exhibit strongly red-shifted and significantly broadened fluorescence spectra, BF$_2$AVB(s) showed unexpectedly sharp emission spectra that can be tuned via the solid form, such as single crystals, dendritic solid, or spin-cast film (Figure 14). The fluorescence color was found to be dramatically altered after crushing or physically smearing BF$_2$AVB crystals or upon scratching or rubbing annealed film samples.
The discovery of an exceptional group of boron-containing compounds, the borolithochromes, causing the distinct pink coloration of well-preserved specimens of the Jurassic red alga Solenopora jurassica, (Figure 15) was reported in [63]. The borolithochromes are characterized as complicated spiroborates (boric acid esters) with two phenolic moieties as boron ligands, representing a unique class of fossil organic pigments. Although the borolithochromes originated from a fossil red alga, no analogy with hitherto known present-day red algal pigments has been found. The occurrence of the borolithochromes or their possible digenetic products in the fossil record may provide additional information on the classification and phylogeny of fossil calcareous algae. Finally, boron measurements at subcellular scale are essential in boron neutron capture therapy (BNCT) of cancer as the nuclear localization of boron-10 atoms can enhance the effectiveness of killing individual tumor cells. Thus, the secondary ion mass spectrometry (SIMS)-based imaging technique of ion microscopy was used [64] to quantitatively image the boron from two BNCT agents, clinically using p-boronophenylalanine (BPA) and 3-carboranylalkylthymidine (N4) (Figure 16) in mitotic metaphase and interphase human glioblastoma T98G cells. N4 belongs to a class of experimental BNCT agents, designated 3-carboranylthymidine analogues (3CTAs), which presumably accumulate selectively in cancer cells due to a process referred to as

![Figure 13](image1.png)

**Figure 13.** (A) Chemical structure of BF₂AVB. (B–D) Photos showing (B) green and (C) cyan crystals, and (D) the blue coral-like solid under UV excitation (λex) 365 nm. (E) SEM image of the dendritic coral-like structure. (F) Magnified view of the porous surface.

![Figure 14](image2.png)

**Figure 14.** Crystal packing for (A) green and (B) cyan BF₂AVB crystals, showing Hirshfeld surfaces of the central molecules mapped with de. The most significant intermolecular interactions are as follows: (A1) C(arene)-H···F hydrogen bond; (A2) C(methyl)-H···π interaction; (A3) short H···H contacts; (B1, B2) C(arene)-H···F hydrogen bonds; (B3) C(methyl)-H···O hydrogen bond; (B4) short H···H contacts.

The discovery of an exceptional group of boron-containing compounds, the borolithochromes, causing the distinct pink coloration of well-preserved specimens of the Jurassic red alga Solenopora jurassica, (Figure 15) was reported in [63]. The borolithochromes are characterized as complicated spiroborates (boric acid esters) with two phenolic moieties as boron ligands, representing a unique class of fossil organic pigments. Although the borolithochromes originated from a fossil red alga, no analogy with hitherto known present-day red algal pigments has been found. The occurrence of the borolithochromes or their possible digenetic products in the fossil record may provide additional information on the classification and phylogeny of fossil calcareous algae. Finally, boron measurements at subcellular scale are essential in boron neutron capture therapy (BNCT) of cancer as the nuclear localization of boron-10 atoms can enhance the effectiveness of killing individual tumor cells. Thus, the secondary ion mass spectrometry (SIMS)-based imaging technique of ion microscopy was used [64] to quantitatively image the boron from two BNCT agents, clinically using p-boronophenylalanine (BPA) and 3-carboranylalkylthymidine (N4) (Figure 16) in mitotic metaphase and interphase human glioblastoma T98G cells. N4 belongs to a class of experimental BNCT agents, designated 3-carboranylthymidine analogues (3CTAs), which presumably accumulate selectively in cancer cells due to a process referred to as
kinase-mediated trapping (KMT). The cells were exposed to BPA for 1 h and N4 for 2 h. The BPA-treated interphase cells revealed significantly lower concentrations of boron in the perinuclear mitochondria-rich cytoplasmic region compared with the remaining cytoplasm and the nucleus, which were not significantly different from each other. In contrast, the BPA-treated metaphase cells revealed a significantly lower concentration of boron than cytoplasm in their chromosomes. In addition, the cytoplasm of metaphase cells contained significantly less boron than the cytoplasm of interphase cells.

\[
\begin{array}{c}
\text{(C}_{25}\text{H}_{15}\text{O})(\text{OH})_3 \\
\text{B} \\
\text{(C}_{25}\text{H}_{15}\text{O})(\text{OH})_3
\end{array}
\]

Figure 15. Structure of the main single isomeric borolithochrome (C_{50}H_{36}O_{12}B,[M] at m/z 839).

![Chemical structures of boronophenylalanine and boronated nucleoside](image)

Figure 16. Chemical structures of boronophenylalanine and boronated nucleoside 55, 3-carboranylalkylthymidine.

4. O-B-N Boronates

A series of boronates 56a–56b were synthesized by the single step reaction of 2,4-pentanedione, aminophenol, and phenylboronic acid in good yield (Scheme 11) \[65\]. The compounds crystallized in centrosymmetric space groups are useful for the growth of organic crystals with luminescent and nonlinear optical properties. The crystals were used to prepare aqueous colloidal nanocrystals that exhibited superior fluorescence properties to those of the boronates when dissolved in organic solvents. This image shows a photograph of the luminescence observed from the colloidal solution (Figure 17); for comparison, this figure also shows the absence of fluorescence from a chloroform solution of 56b with the same molar concentration as the colloidal solution of nanocrystals.
The results showed that the N\textsubscript{58b} compound nonplanar conformation for the main p-backbone, acquired after boron complexation; for diphenylboronic acid (Scheme 13) [69]. Compounds complexes (optimizes the third-order nonlinear optical (NLO) response. In addition, three boron π-coordinative bond facilitates the polarization of the electronic π-system, a situation that optimizes the third-order nonlinear optical (NLO) response. In addition, three boron complexes (65a–65c) were prepared by the reaction of bidentate ligands (66a–66c) and diphenylboronic acid (Scheme 13) [69]. Compounds 58a and 58c were found to have a nonplanar conformation for the main p-backbone, acquired after boron complexation; for compound 58b, the planar conformation is preserved.
They showed large Stokes shifts (mostly above 3200 cm\(^{-1}\)) and in the solid state up to 40%. Introducing a long alkyl chain with a phenyl spacer at this axial position enables the self-assembly of the boron compound to form a fluorescent compound (CPB) as fluorophore. Additionally, boron compound 68d was found to serve as a dye for cell imaging since it has the capability of binding to the nuclear membrane cells. A boron complex bearing a pyrene ligand was synthesized (Scheme 15) and quantum yields in solution and in the solid state fluorescence quantum yields, as well as stable redox properties, indicating that they are possible candidates for emitters and charge transporting materials in electronic devices.

A series of fluorescent boron systems 67a–67c and 68a–68d based on nitrogen (NNN) or nitrogen and oxygen (ONO)-containing tridentate ligands were prepared (Scheme 14) [70]. They showed large Stokes shifts (mostly above 3200 cm\(^{-1}\)) and quantum yields in solution and in the solid state up to 40%. Introducing a long alkyl chain with a phenyl spacer at this axial position enables the self-assembly of the boron compound 68d to form a fluorescent vesicle, which is able to encapsulate small molecules such as sulforhodamine. Additionally, boron compound 68d was found to serve as a dye for cell imaging since it has the capability of binding to the nuclear membrane cells. A boron complex bearing a pyrene ligand

Scheme 12. Synthesis of N,O-containing bororganic compounds 57–60.

Figure 18. Structures of bidentate ligand (63) and boronate (64).

Scheme 13. Synthesis of 65a–65c from 66a–66c and diphenylborinic acid.

![Diagram](image-url)
(CPB) as fluorophore was synthesized (Scheme 15) and introduced as the first example of a binuclear boron complex inorganic light-emitting diode [71]. Complex CPB exhibited strong red-light emission in the solid state. In the polymer light-emitting diodes fabricated with the CPB complex blended with PVK, red emission could be achieved easily by tuning the weight concentration of CPB.

A series of boron ketoiminate derivatives that exhibited clear aggregation-induced emission (AIE) characteristics (in THF, FPL =0.01; in the solid state, FPL = 0.30–0.76) were prepared by the reactions of 1,3-enaminoketone derivatives with boron trifluoride–diethyl etherate (Scheme 16) [72–83]. The boron ketoiminate units can be applied as a new building block of various AIE-active materials. The reaction of 8-hydroxyquinoline (HQ) with B(C$_6$F$_5$)$_3$ led [84–88] to the formation of the zwitterionic compound ($\text{C}_6\text{F}_5$)$_3$BQH (Scheme 17). On the basis of these and other results, it was shown that fluorination of the phenyl rings results in a stabilization of both the HOMO and LUMO levels; therefore, the effect on the absorption and emission maxima in the UV–Vis and PL spectra, respectively, is only minimal. However, the difference in stability and volatility between fluorinated and unfluorinated luminescent boron compounds may have an effect on their solid-state properties and their performance in OLED devices.
Scheme 15. Synthetic route of the compound CPB and its crystal structure.

Scheme 16. Synthetic route to boron ketoiminate 78a–78c.
Among benzoxazole and benzothiazole derivatives, two π-conjugated organoboron complexes 80 and 81 (Figure 19) with rigid seven-ring fused core structures bridged by boron atoms and highly efficient red (632 nm) and deep red (670 nm) solid-state fluorescence were constructed [89–94] (Scheme 18) and qualified as potential nondoped red emitters accompanied by excellent electron-transport ability. The two side phenyl groups coordinated to each boron atom effectively keep the luminescent units apart. As a result, these red fluorophores are brightly fluorescent in the solid state (fluorescence quantum yields: 0.30 for 80 and 0.41 for 81). Their emission spectra are shown (Figure 20). 2-(20-Hydroxyphenyl)benzoxazole (HBO) and 2-(20-hydroxyphenyl)benzothiazole (HBT) reacted with triphenylborane produced two rigid π-conjugated fluorescent cores: 82 (BPh2(BOZ), BOZ 2-(benzo[d]oxazol-2-yl)phenol); 83 (BPh2(BTZ), BTZ 2-(benzo[d]thiazol-2-yl)phenol) [95–99]. Simple modification of these frameworks (Scheme 19) allowed the synthesis of strongly fluorescent materials 84 (BPh2(para-Cz-BTZ), Cz 9H-carbazol-9-yl), 85 (BPh2(para-NPh2-BOZ), NPh2diphenylamino), 86, and 87 (BPh2(para-NMe2-BTZ), NMe2dimethylamino). Organic light-emitting diodes employing these boron complexes as emitters not only kept the full-color tunable emission feature but also showed high electroluminescent performance.

Scheme 15. Synthetic route to boron ketoiminate 80 and 81 with rigid seven-ring fused core structures bridged by boron atoms and highly efficient red (632 nm) and deep red (670 nm) solid-state fluorescence were constructed [89–94] (Scheme 18) and qualified as potential nondoped red emitters accompanied by excellent electron-transport ability. The two side phenyl groups coordinated to each boron atom effectively keep the luminescent units apart. As a result, these red fluorophores are brightly fluorescent in the solid state (fluorescence quantum yields: 0.30 for 80 and 0.41 for 81). Their emission spectra are shown (Figure 20). 2-(20-Hydroxyphenyl)benzoxazole (HBO) and 2-(20-hydroxyphenyl)benzothiazole (HBT) reacted with triphenylborane produced two rigid π-conjugated fluorescent cores: 82 (BPh2(BOZ), BOZ 2-(benzo[d]oxazol-2-yl)phenol); 83 (BPh2(BTZ), BTZ 2-(benzo[d]thiazol-2-yl)phenol) [95–99]. Simple modification of these frameworks (Scheme 19) allowed the synthesis of strongly fluorescent materials 84 (BPh2(para-Cz-BTZ), Cz 9H-carbazol-9-yl), 85 (BPh2(para-NPh2-BOZ), NPh2diphenylamino), 86, and 87 (BPh2(para-NMe2-BTZ), NMe2dimethylamino). Organic light-emitting diodes employing these boron complexes as emitters not only kept the full-color tunable emission feature but also showed high electroluminescent performance.

Figure 19. The design strategy towards diboron-containing complexes with a seven-ring fused π-conjugated skeleton (a) R = Fluorene based 2-(2'-hydroxyphenyl)benzoxazole and 2-(2'-hydroxyphenyl)benzothiazole ligands. (b) scheme of formation of fluorescent red and deep red boron containing complex.
Scheme 18. Synthetic routes to the boron complexes 82–85.

Figure 20. Emission spectra (a) and photographs under UV light (365 nm) (b) of 82–85 in CH$_2$Cl$_2$ and the solid state.
Complexation of boron trifluoride by a series of electron donor/acceptor substituted 2-(20-hydroxy phenyl) benzoxazole (HBO) derivatives resulted in luminescent B(III) complexes 106–114 (Scheme 19) with an emission wavelength ranging from 385 to 425 nm in dichloromethane or toluene [100]. Depending on the nature of the substituents present on the core of the starting substituted 2-aminophenol I and 2-hydroxybenzaldehyde II, two different routes were chosen. Route A involved refluxing I and II together in ethanol to obtain the cyclic carbinolamines, which precipitated from the reaction mixture (Scheme 20). After collection, these compounds were oxidized with slight excess of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). The second one-pot route B involves the oxidation-sensitive substituents, such as diethylamino groups, in presence of phenylboronic acid and requires potassium cyanide to promote benzoxazole cyclization. The synthesized dyes can be connected to other photoactive subunits such as BODIPY or Boranil cores to afford sophisticated molecular cassettes. In addition, four diboron-bridged, π-conjugated ladder molecules 115 were designed (Figure 21) and synthesized (Scheme 21) [101]. It was revealed that the bulky phenyl substituents on boron centers efficiently prevented π stacking of the luminescent ladder unit. The construction of diboron-containing ladder-type skeletons endowed these materials with good thermal stability, high fluorescence quantum yields, and strong electron affinity. Simple EL devices fabricated using complexes 116 and 117 as both emitter- and electron-transporting materials exhibited the highest brightness and efficiency among boron-containing materials reported so far. Finally, fluorescent homopolymers and amphiphilic block copolymers were prepared by reversible addition–fragmentation chain transfer (RAFT) polymerization of two styryl-type organoboron monomers (Scheme 22) [102–105]. Block copolymers featuring a relatively long PEO segment formed stable micellar solutions in water with luminescence characteristics similar to those of the respective (water-insoluble) homopolymers, suggesting potential applications as nanosized fluorophores in biological environments.
Scheme 20. Synthesis of substituted 2-(20-hydroxyphenyl)-benzoxazole (HBO) 97–105 derivatives and their corresponding B(III) complexes 106–114.

Figure 21. Design of a strategy toward a diboron-containing ladder 115.
“push–pull” type of molecules [106–108]. These compounds derive from the well-known stilbene backbone, to which an arylboron (ArB) fragment has been added. This family of readily available macrocyclic boron compounds has recently attracted some interest from various perspectives in analytical and supramolecular chemistry. Thus, a series of eighteen such molecules were obtained by self-assembly of salicylideniminophenols and various phenylboronic acids [109–114]. Such compounds can be prepared according to the reactions where a monomeric boronate and an oxobridged chiral dimer were obtained by reaction of the ligand derived from 4-diethylaminosalicylaldehyde with (R)-(R)-phenylglycinol and phenyl boronic acid or boric acid (Table 1) [115–121]. The existence of the N–B coordination bond was established by 11B NMR, which showed the characteristic signal at 4.0, 2.1 ppm for 125, 6.1 ppm for 126, and 6.1 ppm for 126, respectively (Scheme 23). Electric-field-induced second-harmonic measurements of the nonlinear optical response revealed that the nature of the phenyl-boron moieties has a modest influence on the molecular hyperpolarizabilities.
Table 1. Table for preparation of various salicylideniminophenols.

| R₁  | R₂  | R₃  | R₄  | R₅  | R₆  | R₁  | R₂  | R₃  | R₄  | R₅  | R₆  |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| OMe | H   | H   | H   | H   | H   | 1a  | H   | H   | H   | H   | H   | 2a  |
| H   | NO₂ | H   | H   | H   | H   | 1b  | H   | NO₂ | H   | H   | H   | 2b  |
| F   | F   | F   | F   | F   | F   | 1c  | F   | F   | F   | F   | F   | 2c  |
| F   | H   | F   | H   | H   | H   | 1d  | F   | H   | F   | H   | H   | 2d  |
| H   | Cl  | H   | H   | H   | H   | 1e  | H   | Cl  | H   | H   | H   | 2e  |
| H   | H   | Cl  | H   | H   | 1f  | H   | H   | Cl  | H   | H   | 2f  |
| H   | H   | Me  | H   | H   | 1g  | H   | H   | Me  | H   | H   | 2g  |
| H   | OMe | H   | H   | H   | H   | 1h  | H   | OMe | H   | H   | H   | 2h  |

Scheme 23. Synthesis of boronates 122a, 123b, and 124.

Solvent effects on the spectroscopic and photophysical properties of tris([p-(N,N-dimethylamino)phenylethynyl]-duryl]borane (TMAB) and tris([phenylethynyl]duryl]borane (TPhB) (Figure 22) were studied [122–135]. Both TMAB and TPhB exhibited broad and structureless absorption and fluorescence bands attributed to the charge transfer (CT) transition between the π-orbital of the aryl group (π(aryl)) and the vacant p-orbital on the boron atom (p(B)): π(aryl)-p(B) CT.

Figure 22. Structures of TMAB and TPhB.
5. Conclusions

In this review, we summarized various synthetic methods of BODIPY-based organoboron compounds with different frameworks. We also summarized the various optical and non-linear properties of these compounds along with their applications. BODIPY compounds based on NBN network were synthesized by Liebeskind–Srogl; Liebeskind–Srogl and Suzuki coupling showed intense absorption and large Stokes, unlike the typical BODIPY due to the geometry relaxation. The DFT calculations supported the geometrical relaxation upon photoexcitation and its remarkable effect on the energy levels of molecular orbitals. Moreover, boron compounds containing O-B-O upon interaction with aggregates increase the fluorescence by 70-fold to 90 nm blue shift and significantly increase in quantum yield. New compounds such as the boron dodecane complex (BF$_2$ dbmOC$_{12}$H$_{25}$) have emerged with dependent and reversible mechanochromic fluorescence.

A series of fluorescent boron systems based on nitrogen (NNN) or nitrogen and oxygen (ONO)-containing tridentate ligands were reported. They showed large Stokes shifts and quantum yields in solution and in the solid state. Introducing a long alkyl chain with a phenyl spacer at this axial position enables the self-assembly of the boron compound to form a fluorescent vesicle, which is able to encapsulate small molecules such as sulforhodamine. Furthermore, few boron compounds were found to serve as a dye for cell imaging since it has the capability of binding to the nuclear membrane cells. Moreover, a boron complex bearing a pyrene ligand (CPB) as fluorophore was synthesized and introduced as the first example of a binuclear boron complex inorganic light-emitting diode. Complex CPB exhibited strong red-light emission in the solid state. In the polymer light-emitting diodes fabricated with the CPB complex blended with PVK, red emission could be achieved easily by tuning the weight concentration of CPB.

Finally, fluorescent homopolymers and amphiphilic block copolymers were prepared by reversible addition–fragmentation chain transfer (RAFT) polymerization of two styryl-type organoboron monomers. Block copolymers featuring a relatively long PEO segment formed stable micellar solutions in water with luminescence characteristics similar to those of the respective homopolymers, suggesting potential applications as nanosized fluorophores in biological environments.

Author Contributions: Conceptualization, original draft preparation, review and editing and project administration P.M.G., V.M.J.P. and N.S.H.; investigation and resources, B.M.M.-F.; formal analysis V.P.S.; All authors have read and agreed to the published version of the manuscript.

Funding: This research study was funded by the PAICYT (Grant: CE-1721-21), Chemistry Faculty-UANL for the financial support, VGST, Govt. of Karnataka for VGST-SMYSR (GRD 503), VGST KFIST L-1 (GRD 952), RCU for Minor Research Project (2019 and 2020 respectively) and DST for DST-FIST grant.

Conflicts of Interest: The authors declare no conflict of interest.

Sample Availability: Samples of the compounds are not available from the authors.

References
1. James, T.D.; Shinkai, S. Saccharide-Selective Boronic Acid Based Photoinduced Electron Transfer (PET) Fluorescent Sensors. Top. Curr. Chem. 2002, 218, 159.
2. Jelinek, R.; Kolusheva, S. Carbohydrate biosensor. Chem. Rev. 2004, 104, 5987–6015. [CrossRef] [PubMed]
3. Pal, A.; Berube, M.; Hall, D.G. Design, Synthesis, and Screening of a Library of Peptidyl Bis(Boroxoles) as Oligosaccharide Receptors in Water: Identification of a Receptor for the Tumor Marker TF-Antigen Disaccharide. Angew. Chem. Int. Ed. 2010, 49, 1492–1495. [CrossRef] [PubMed]
4. Hansen, J.S.; Christensen, J.B.; Petersen, J.F.; HoegJensen, T.; Norrild, J.C. Arylboronic acids: A diabetic eye on glucose sensing. Sens. Actuators B 2012, 161, 45–79. [CrossRef]
5. Wade, C.R.; Broomsgrove, A.J.; Aldridge, S.; Gabbai, F.P. Fluoride Ion Complexation and Sensing Using Organoboron Compounds. Chem. Rev. 2010, 110, 3958–3984. [CrossRef] [PubMed]
6. Wu, X.; Li, Z.; Chen, X.-X.; Fossey, J.S.; James, T.D.; Jiang, Y.B. Selective sensing of saccharides using simple boronic acids and their aggregates. Chem. Soc. Rev. 2013, 42, 8032–8048. [CrossRef] [PubMed]
34. Roacho, R.I.; MetaMagana, A.J.; PeÇa-Cabrera, E.; Pannell, K.H. Synthesis, structural characterization, and spectroscopic properties of the ortho, meta, and para isomers of 8-(HOCH$_2$-C$_6$H$_2$)-BODIPY and 8-(MeOC$_6$H$_4$)-BODIPY. *J. Phys. Org. Chem.* 2013, 26, 345–351. [CrossRef]

35. Martinez-Gonzalez, M.R.; Urias-Benavides, A.; AlvaradoMartinez, E.; Lopez, J.C.; Gjmez, A.M.; del Rio, M.; Garcia, I.; Costela, A.; BaÇuelos, J.; Arbeloa, T.; et al. Conventional Access to Carbohydrate–BODIPY Hybrids by Two Complementary Methods Involving One-Pot Assembly of “Clickable” BODIPY Dyes. *Eur. J. Org. Chem.* 2014, 7659–7663. [CrossRef]

36. Karolin, J.; Johansson, B.A.L.; Strandberg, J.; NyZ, T. Fluorescence and Absorption Spectroscopic Properties of Dipyrromethen-eboron Difluoride (BODIPY) Derivatives in Liquids, Lipid Membranes, and Proteins. *J. Am. Chem. Soc.* 1994, 116, 7801–7806. [CrossRef]

37. Loutet, A.; Burgess, K. BODIPY Dyes and Their Derivatives: Syntheses and Spectroscopic Properties. *Chem. Rev.* 2007, 107, 4891–4932. [CrossRef] [PubMed]

38. Leen, V.; Miscoria, D.; Yin, S.; Filarowski, A.; Ngongo, J.M.; Auweraer, M.V.; Boens, N.; Dehaen, W. 1,7-Disubstituted Boron Difluoride-Derivatives in Liquids, Lipid Membranes, and Proteins. *J. Am. Chem. Soc.* 2010, 132, 8168–8176. [CrossRef]

39. Chen, Y.; Zhao, J.; Guo, H.; Xie, L. Geometry Relaxation-Induced Large Stokes Shift in Red-Emitting Borondipyromethene (BODIPY) and Applications in Fluorescent Thiol Probes. *J. Org. Chem.* 2012, 77, 2192–2206. [CrossRef]

40. Lakowicz, J.R. *Principles of Fluorescence Spectroscopy*, 2nd ed.; Kluwer Academic: New York, NY, USA, 1999.

41. Valeur, B. Molecular Fluorescence: Principles and Applications; Wiley-VCH Verlag: Weinheim, Germany, 2001.

42. Chibani, S.; LeGuennic, B.; Charaf-Eddin, A.; Maury, O.; Andraud, C.; Jacquemin, D. On the computaional of asiabatic energies of the BODIPY dye. *J. Phys. Org. Chem.* 2012, 8, 3303–3313.

43. Küköz, B.; Hayvalı, K.; Yılmaz, M.; U’guz, H.; Ulas, B.; Kürim, U.; Gul Yaglioglu, H.; Elmalı, A. Synthesis, optical properties and ultrafast dynamics of aza-boron-dipyrromethene compounds containing methoxy and hydroxy groups and two-photon absorption cross-section. *J. Photochem. Photobiol. A Chem.* 2012, 247, 24–29. [CrossRef]

44. Liu, Y.; Kong, M.; Zhang, Z.; Zhou, H.; Zhang, S.; Li, S.; Wu, J.; Tian, Y. A series of triphenylamine-based two-photon absorbing materials with AIE property for biological imaging. *J. Mater. Chem. B* 2014, 2, 5430–5440. [CrossRef]

45. Du, M.L.; Hu, C.Y.; Wang, L.F.; Li, C.; Han, Y.Y.; Gan, X.; Chen, Y.; Mu, W.H.; Huang, M.L.; Fu, W.F. New members of fluorescent 1,8-naphthyridine-based BF$_2$ compounds: Selective binding of BF$_2$ with terminal bidentate N’N’ and N’C’ groups and tunable spectroscopy properties. *Dalton Trans.* 2014, 43, 13924–13931. [CrossRef] [PubMed]

46. Anareda, J.F.; Piers, W.E.; Heyne, B.; Parvez, M.; McDonald, R. Progress in the Science of Functional Dyes. *Angew. Chem. Int. Ed.* 2011, 50, 1–5.

47. Wang, Y.; Zhang, D.; Zhou, H.; Ding, J.; Chen, Q.; Yao, X.; Qian, S. Nonlinear optical properties and ultrafast dynamics of three novel boradiazaizindacene derivatives. *J. Appl. Phys.* 2010, 8, 33–520. [CrossRef]

48. Kowada, T.; Yamaguchi, S.; Ohe, K. Highly Fluorescent BODIPY Dyes Modulated with Spirolfluorene Moieties. *Org. Lett.* 2010, 12, 296–299. [CrossRef]

49. Mathew, T.W.; Patel, N.M.; Roberts, S.T.; Kathryan, A.; Djurovich, I.P.; Bradforth, E.S.; Thompson, M.E. Symmetry-breaking intramolecular charge transfer in the excited state of meso-linked BODIPY dyads. *Chem. Commun.* 2012, 48, 284–286.

50. Li, Z.; Lin, T.; Liu, S.; Huang, C.; Hudnall, T.W.; Gabbai, F.P.; Conti, P.S. Rapid aqueous [BF$_4$]$^-$ labeling of a bodipy dye for positron emission tomography/fluorescence dual modality imaging. *Chem. Commun.* 2011, 47, 9324–9326. [CrossRef]

51. Kim, T.; Park, J.; Park, S.; Choi, Y.; Kim, Y. Visualization of tyrosinase activity in melanoma cells by a BODIPY-based fluorescent probe. *Chem. Commun.* 2011, 47, 12640–12642. [CrossRef]

52. Tokoro, Y.; Nagai, A.; Chuo, Y. Luminescent chiral organoboron 8-aminoquininolate-coordination polymers. *Appl. Organomet. Chem.* 2010, 24, 563–568. [CrossRef]

53. Tsumenasa, N.; Tsuobu, A.; Okamura, H. Effects of Organoboron Antifoulants on Oyster and Sea Urchin Embryo Development. *Int. J. Mol. Sci.* 2013, 14, 421–433. [CrossRef]

54. Martens, S.C.; Riehm, T.; Wadepohl, H.; Gade, L.H. Tetra-N-silylated Bis(borylene)tetraaminoperylenes (“DIBOTAPs”): Synthesis, Structures and Photophysics. *Eur. J. Inorg. Chem.* 2012, 18, 3039–3046. [CrossRef]

55. Bolze, F.; Hayek, A.; Sun, X.H.; Baldeck, P.L.; Bourgogne, C.; Nicoud, J.-F. New insight in boron chemistry: Application in two-photon absorption. *Opt. Mater.* 2011, 33, 1453–1458. [CrossRef]

56. Mirochnik, A.G.; Fedorenko, E.V.; Gizzatulina, D.K.; Karasev, V.E. Photoinduced enhancement of luminescence from (dibenzoylmethanato)boron difluoride in polymethyl methacrylate. *Russ. J. Phys. Chem.* 2007, 81, 1880–1883. [CrossRef]

57. Ran, C.; Xu, X.; Raymond, S.B.; Ferrara, B.J.; Neal, K.; Bacskaï, B.J.; Medarova, Z.; Moore, A. Design, Synthesis, and Testing of Difluoroboron-Derivatized Curcuminoids as Near-Infrared Probes for in Vivo Detection of Amyloid-β Deposits. *J. Am. Chem. Soc.* 2009, 131, 15257–15261. [CrossRef] [PubMed]

58. Zhang, G.; Singer, J.P.; Kooi, S.E.; Evans, R.E.; Thomas, E.L.; Fraser, C.L. Reversible solid-state mechanochromic fluorescence from a boron lipid dye. *J. Mater. Chem.* 2011, 21, 8295. [CrossRef]

59. Zhang, G.; Lu, J.; Sabat, M.; Fraser, C.L. Polymorphism and Reversible Mechanochromic Luminescence for Solid-State Difluoroboron Avobenzene. *J. Am. Chem. Soc.* 2010, 132, 2160–2162. [CrossRef]

60. Nguyen, N.D.; Zhang, G.; Lu, J.; Sherman, A.E.; Fraser, C.L. Alkyl chain length effects on solid-state difluoroboron β-diketonate mechanochromic luminescence. *J. Mater. Chem.* 2011, 21, 8409. [CrossRef]
61. Wang, Z.; Wang, M.; Peng, J.; Xie, Y.; Liu, M.; Gao, W.; Zhou, Y.; Huang, X.; Wu, H. Polymorphism and multicolor mechanofluorochromism of a D-π-A asymmetric 4H-pyran derivative with aggregation-induced emission property. J. Phys. Chem. B 2019, 123, 27742–27751.

62. Walkenstein, K.; Gross, J.H.; Falk, H. Boron-containing organic pigments from a Jurassic red alga. Proc. Natl. Acad. Sci. USA 2010, 107, 19374–19378. [CrossRef]

63. Chandra, S.; Jraka, W.; Loretand, D.R.; Barth, R.F. Quantitative subcellular imaging of boron compounds in individual mitotic and interphase human glioblastoma cells with imaging secondary ion mass spectrometry (SIMS). J. Microsc. 2008, 229, 92–103. [CrossRef]

64. Rodrigues, M.; Ramos-Ortiz, G.; Martha, I.; Alcalá-Salas, M.I.; Maldonado, J.L.; López-Varela, K.; López, Y.; Domínguez, O.; Meneses-Nava, M.A.; Barbosa-García, O.; et al. One-pot synthesis and characterization of novel boronates for the growth of single crystals with nonlinear optical properties. Dyes Pigments 2010, 87, 76–83. [CrossRef]

65. He, Z.; Trincher, P.; Adam, S.; Denis, J.D.S.; Andrei, K.; Yudin, K.A. Oxidative geminal functionalization of organoboron compounds. Chem. Int. Ed. 2012, 51, 11092–11096. [CrossRef]

66. Zhang, Z.; Bi, H.; Zhang, Y.; Yao, D.; Gao, H.; Fan, Y.; Zhang, H.; Wang, Y.; Wang, Y.; Chen, Z.; et al. Luminescent Boron-Containing Ladder-Type π-Conjugated Compounds. ACS Inorg. Chem. 2009, 48, 7230–7236. [CrossRef] [PubMed]

67. Rodríguez, M.; Castro-Beltran, R.; Ramos-Ortiz, G.; Maldonado, J.L.; Farfan, N.; Domínguez, O.; Rodríguez, J.; Santillanc, R.; Meneses-Nava, M.A.; Barbosa-García, O.; et al. Synthesis and third-order nonlinear optical studies of a novel four-coordinated organoboron derivative and a bidentate ligand: The effect of the N–B coordinate bond. Synth. Met. 2009, 159, 1281–1287. [CrossRef]

68. Rodríguez, M.; Maldonado, J.L.; Ramos-Ortiz, G.; Domínguez, O.; Ochoa, M.E.; Santillan, R.; Farfan, N.; Meneses-Nava, M.; Barbosa-García, O. Synthesis, X-ray diffraction analysis, and chemical-optical characterizations of boron complexes from bidentate ligands. Polyhedron 2012, 43, 194–200. [CrossRef]

69. Glotzbach, C.; Kauscher, U.; Voskuhl, J.; SedaKehr, N.; Stuart, M.C.A.; Fröhlich, R.; Galla, H.J.; Ravoo, B.J.; Nagura, K.; Saito, M.; et al. Fluorescent Modular Boron Systems Based on NNN- and ONO-Tridentate Ligands: Self-Assembly and Cell Imaging. J. Org. Chem. 2013, 78, 4410–4418. [CrossRef] [PubMed]

70. Zhou, Y.; Kim, J.; Kim, M.J.; Son, W.; Han, S.J.; Kim, H.N.; Han, S.; Kim, Y.; Lee, C.; Kim, S.; et al. Novel Bi-Nuclear Boron Complex with Pyrene Ligand: Red-Light Emitting as well as Electron Transporting Material in Organic Light-Emitting Diodes. Org. Lett. 2010, 12, 1272–1275. [CrossRef]

71. Yoshii, R.; Nagai, A.; Tanaka, K.; Chudo, Y. Highly Emissive Boron Ketoiminate Derivatives as a New Class of Aggregation-Induced Emission Fluorophores. Chem. Eur. J. 2013, 19, 4506–4512. [CrossRef]

72. Tang, C.W.; VanSlyke, S.A. Organic electroluminescent diodes. Appl. Phys. Lett. 1987, 51, 913–915. [CrossRef]

73. Friend, R.H.; Gymer, R.W.; Holmes, A.B.; Burroughes, J.H.; Marks, R.N.; Talian, C.; Bradley, D.D.C.; Dos Santos, D.A.; Brda, J.L.; Lcgdlund, M.; et al. Electroluminescence in conjugated polymers. Nature 1999, 397, 121–128. [CrossRef]

74. Jenekhe, S.A.; Osaheni, J.A. Excimers and Exciplexes of Conjugated Polymers. Science 1994, 265, 765–768. [CrossRef]

75. Luo, J.; Xie, Z.; Lam, J.W.Y.; Cheng, L.; Chen, H.; Qiu, C.; Kwok, H.S.; Zhan, X.; Liu, Y.; Zhu, D.; et al. Aggregation-induced emission of 1-methyl-1,2,3,4,5-pentaphenylsilole. Chem. Commun. 2003, 108, 7522–7526. [CrossRef] [PubMed]

76. Chen, J.; Law, C.C.W.; Lam, J.W.Y.; Dong, Y.; Lo, S.M.F.; Williams, I.D.; Zhu, D.; Tang, B.Z. Synthesis, Light Emission, Nanoaggregation, and Restricted Intramolecular Rotation of 1,1-Substituted 2,3,4,5-Tetraphenylsiloles. Macromolecules 2003, 36, 1535–1546. [CrossRef]

77. Chen, J.; Xie, Z.; Lam, J.W.Y.; Law, C.C.W.; Tang, B.Z. Silole-Containing Polyacetylenes. Synthesis, Thermal Stability, Light Emission, Nanodimensional Aggregation, and Restricted Intramolecular Rotation. Macromolecules 2003, 36, 1108–1117. [CrossRef]

78. Chen, J.; Xu, B.; Ouyang, X.; Tang, B.Z.; Cao, Y. Aggregation-Induced Emission of cis, cis-1,2,3,4-Tetraphenylbutadiene from Restricted Intramolecular Rotation. J. Phys. Chem. A 2004, 108, 7522–7526. [CrossRef]

79. Hong, Y.; Lam, J.W.Y.; Sung, H.H.Y.; Williams, I.D.; Sun, J.Z.; Tang, B.Z. Tunable aggregation-induced emission of diphenyldibenzo[1,4]fulvenes. Chem. Commun. 2006, 10, 1133–1135. [CrossRef] [PubMed]

80. Hong, Y.; Lam, J.W.Y.; Sung, H.H.Y.; Williams, I.D.; Sun, J.Z.; Tang, B.Z. Fluorescent “light-up” bioprobes based on tetraphenylethylene derivatives with aggregation-induced emission characteristics. Chem. Commun. 2006, 35, 3705–3707. [CrossRef]

81. Zeng, Q.; Li, Z.; Dong, Y.; Di, Q.; Qin, A.; Hong, Y.; Zhu, J.; Zhu, Z.; Jim, C.K.W.; Yu, G.; et al. Fluorescence enhancements of benzene-cored luminophors by restricted intramolecular rotations: AIE and AIEE effects. Chem. Commun. 2007, 1, 70–72. [CrossRef]

82. Hong, Y.; Lam, J.W.Y.; Tang, B.Z. Aggregation-induced emission: Phenomenon, mechanism and applications. Chem. Commun. 2009, 29, 4332–4335. [CrossRef]

83. Hellström, J.S.; Britovsek, G.J.P.; Jones, T.S.; Hunt, P.; White, A.J.P. Synthesis and characterisation of luminescent fluorinated organoboron compounds. Dalton Trans. 2007, 14, 1425–1432. [CrossRef]

84. Mullen, K.; Scherf, U. (Eds.) Organic Light Emitting Devices; Wiley-VCH: Weinheim, Germany, 2005.

85. Casas, J.M.; Falcó, L.R.; Forné, J.; Martin, A.; Welch, A.J. Pentfluorophenyl complexes of platinum containing intramolecular Pt–H hydrogen bridging interactions. Crystal structures of [NBu₄][Pt(C₅F₅)₃(8-hydroxyquinidine)] and [NBu₄][Pt(C₅F₅)₃(8-methylquinoline)]. Inorg. Chem. 1996, 35, 6009–6014. [CrossRef]
86. Chen, C.H.; Shi, J. Metal chelates as emitting materials for organic electroluminescence. Coord. Chem. Rev. 1998, 171, 161. [CrossRef]
87. Wang, S. Luminescence and electroluminescence of Al(III), B(III), Be(II) and Zn(II) complexes with nitrogen donors. Coord. Chem. Rev. 2001, 195, 215. [CrossRef]
88. Li, D.; Wang, K.; Huang, S.; Qu, S.; Liu, X.; Zhu, Q.; Zhang, H.; Wang, J.Y. Brightly fluorescent red organic solids bearing boron-bridged π-conjugated skeletons. Mater. Chem. 2011, 21, 15298–15304. [CrossRef]
89. Kim, Y.; Bouffard, J.; Kooi, S.E.; Swager, T.M. Highly Emissive Conjugated Polymer Excimers. J. Am. Chem. Soc. 2005, 127, 13726. [CrossRef]
90. Wakamiya, A.; Mori, K.; Yamaguchi, S. 3-Boryl-2,2′-bithiophene as a Versatile Core Skeleton for Full-Color Highly Emissive Organic Solids. Angew. Chem. Int. Ed. 2007, 46, 4273. [CrossRef] [PubMed]
91. Ye, S.; Chen, J.; Di, C.; Liu, Y.; Lu, K.; Wu, W.; Du, C.; Liu, Y.; Shuai, Z.; Yu, G. Phenyl-substituted fluorene-dimer cored anthracene derivatives: Highly fluorescent and stable materials for high performance organic blue- and white-light-emitting diodes. J. Mater. Chem. 2010, 20, 3186–3194. [CrossRef]
92. Yao, Y.-S.; Zhou, Q.-Z.; Wang, X.-S.; Wang, Y.; Zhang, B.-W. Fine tuning of the photophysical and electroluminescent properties of DCM-type dyes by changing the structure of the electron-donating group. J. Mater. Chem. 2006, 16, 3512. [CrossRef]
93. Odom, S.A.; Parkin, S.R.; Anthony, J.E. Tetracene Derivatives as Potential Red Emitters for Organic LEDs. Org. Lett. 2003, 5, 4245–4248. [CrossRef]
94. Li, D.; Zhang, H.; Wang, C.; Guo, J.; Wang, Y. Construction of full-color-tunable and strongly emissive materials by functionalizing a boron-chelate four-ring-fused π-conjugated core. J. Mater. Chem. 2012, 22, 4319–4328. [CrossRef]
95. Satrijo, A.; Kooi, S.E.; Swager, T.M. Enhanced luminescence from emissive defects in aggregated conjugated polymers. Macromolecules. 2007, 40, 8833–8841. [CrossRef]
96. Vidyasagar, C.C.; Muñoz Flores, B.M.; Jiménez-Pérez, V.M.; Gurubasavaraj, P.M. Recent advances in boron-based Schiff base derivatives for organic light-emitting diodes. Mater. Today Chem. 2018, 11, 133–155. [CrossRef]
97. Wu, Z.; Wang, Q.; Yu, L.; Chen, J.; Qiao, X.; Ahamad, T.; Alshehri, S.M.; Yang, C.; Ma, D. Managing excitons and charges for high-performance fluorescent white organic light-emitting diode. ACS Appl. Mater. Interfaces 2016, 8, 28780–28788. [CrossRef] [PubMed]
98. Jung, B.J.; Yoon, C.-B.; Shim, H.-K.; Do, L.-M.; Zyung, T. Pure-Red Dye for Organic Electroluminescent Devices: Bis-Condensed DCM Derivatives. Adv. Funct. Mater. 2013, 23, 1143. [CrossRef]
99. Massue, J.; Denis, F.; Ulrich, G.; Retailleau, P.; Ziessel, R. Synthesis of Luminescent 2-(2-Hydroxyphenyl)benzoxazole (HBO) Borate Complexes. Org. Lett. 2012, 14, 230–233. [CrossRef] [PubMed]
100. Li, D.; Yuan, Y.; Bi, H.; Yao, D.; Zhao, X.; Tian, W.; Wang, Y.; Zhang, H. Boron-Bridged π-Conjugated Ladders as Efficient Electron-Transporting Emitters. Inorg. Chem. 2011, 50, 4825–4831. [CrossRef]
101. Cheng, F.; Jäkle, F. RAFT polymerization of luminescent boron quinolate monomers. Chem. Commun. 2010, 46, 3717–3719. [CrossRef]
102. Matsumi, N.; Chujo, Y. π-Conjugated Organoboron Polymers via the Vacant p-Orbital of the Boron Atom. Polym. J. 2008, 40, 77–89. [CrossRef]
103. Elbing, M.; Bazan, G.C. A New Design Strategy for Organic Optoelectronic Materials by Lateral Boryl Substitution. Angew. Chem. Int. Ed. 2008, 47, 834–838. [CrossRef]
104. Jäkle, F. Lewis acidic organoboron polymers. Coord. Chem. Rev. 2006, 250, 1107–1121. [CrossRef]
105. Lamère, J.F.; Lacroix, P.G.; Farfa, N.; Rivera, J.M.; Santillan, R.; Nakatani, K. Synthesis, characterization and nonlinear optical (NLO) properties of a push–pull bisboronate chromophore with a potential electric field induced NLO switch. J. Mater. Chem. 2006, 16, 2913–2920. [CrossRef]
106. Maldonado, J.L.; Ramos-Ortíz, G.; Barbosa-García, O.; Meneses-Nava, M.A.; Arquez, L.M.; Olmos-Lope, M. Dynamic holographic imaging using photorefractive polymers based on a boronate-derivative non-linear chromophore. Int. J. Mod. Phys. B 2007, 21, 2625–2634. [CrossRef]
107. Shi, W.-J.; Lo, P.-C.; Singh, A.; Ledoux-Rak, I.; Ng, D.K.P. Synthesis and second-order nonlinear optical properties of push-pull BODIPY derivatives. Tetrahedron. 2012, 68, 8712–8718. [CrossRef]
108. Reyes, H.; Muñoz, B.M.; Farfán, N.; Santillan, R.; Rojas-Lima, S.; Lacroix, P.G.; Nakatani, K. Synthesis, crystal structures, and quadratic nonlinear optical properties in a series of push–pull boronate derivatives. J. Mater. Chem. 2002, 12, 2898–2903. [CrossRef]
109. Prasad, P.N.; Williams, D.J. (Eds.) Introduction to Nonlinear Optical Effects in Molecules and Polymers; Wiley: New York, NY, USA, 1991.
110. Kuhn, H.; Robillard, J. (Eds.) Nonlinear Optical Materials; CRC Press: Boca Raton, MIA, USA, 1992.
111. Nalwa, H.S.; Miyata, S. (Eds.) Nonlinear Optics of Organic Molecules and Polymers; CRS Press: New York, NY, USA, 1997.
112. Verbiest, T.; Houbrechts, S.; Kauranen, M.; Clays, K.; Persoons, A. Second-order nonlinear optical materials: Recent advances in chromophore design. J. Mater. Chem. 1997, 7, 2175–2189. [CrossRef]
113. Dalton, L.R.; Harper, A.W.; Ghosh, R.; Steier, W.H.; Ziairi, M.; Fetterman, H.; Shi, Y.; Mustacich, R.V.; Jen, A.K.-Y.; Shea, K.J. Synthesis and Processing of Improved Organic Second-Order Nonlinear Optical Materials for Applications in Photonics. Chem. Mater. 1995, 7, 1060. [CrossRef]
114. Reyes, H.; Rivera, J.M.; Farfán, N.; Santillan, R.; Lacroix, P.G.; Lepetit, C.; Nakatani, K. Synthesis and quadratic molecular hyperpolarizabilities of two new chiral boronates: Computational and experimental study. J. Organomet. Chem. 2005, 690, 3737–3745. [CrossRef]

115. Hawthorne, M.F.; Lee, M.W. A Critical Assessment of Boron Target Compounds for Boron Neutron Capture Therapy. J. Neurooncol. 2003, 62, 33. [CrossRef]

116. Sakuda, E.; Ando, Y.; Ito, A.; Kitamura, N. Extremely Large Dipole Moment in the Excited Singlet State of Tris[(p-(N,N-dimethy lamino)phenylethynyl)dimethylamino]duryl]borane. J. Phys. Chem. A 2010, 114, 9144–9150. [CrossRef] [PubMed]

117. Kennedy, J.W.J.; Hall, D.G. Recent Advances in the Activation of Boron and Silicon Reagents for Stereocontrolled Allylation Reactions. Angew. Chem. Int. Ed. 2003, 42, 4732. [CrossRef]

118. Liu, Z.; Fang, Q.; Cao, D.; Wang, D.; Xu, G. Triaryl Boron-Based A-(Diarylboryl)phenyl-Substituted 2,7- and 3,6-Linked π-Conjugated Polymers via Grignard Reagent. Org. Lett. 2004, 6, 2933. [CrossRef]

119. Entwistle, C.D.; Marder, T.B. Boron Chemistry Lights the Way: Optical Properties of Molecular and Polymeric Systems. Acc. Chem. Res. 2009, 42, 3488–3492. [CrossRef]

120. Candeias, N.R.; Montalbano, F.; Cal, P.M.S.D.; Gois, P.M. Boronic acid and esters in the petasis-boron manchin multicomponent reaction. Chem. Rev. 2010, 10, 6169–6193. [CrossRef] [PubMed]

121. Doglietto, G.; Moro, M.; Togni, A.; Rizzitano, G.; Trinchieri, C. β-Boronic Acids: From Isolation to Synthesis. Eur. J. Org. Chem. 2009, 4041–4059. [CrossRef]

122. Miller, D.S.; Leffler, J.E. Absorption spectra of triarylborons. J. Phys. Chem. 1970, 74, 2571. [CrossRef]

123. Matsumi, N.; Naka, K.; Chujo, Y. J. Am. Chem. Soc. 1998, 120, 10776. [CrossRef]

124. Matsumi, N.; Kotera, K.; Chujo, Y. Alternating Boration Copolymerization between Diynes and Diisocyanates. Organoboron Polymers Bearing Monomeric Iminoborane in Their Main Chain. Macromolecules 2000, 33, 2801–2806. [CrossRef]

125. Matsumi, N.; Umeyama, T.; Chujo, Y. π-Conjugated poly (cycloborazane) s with intramolecular charge transferred structure. Macromolecules 2000, 33, 3956–3957. [CrossRef]

126. Matsumi, N.; Chujo, Y. Synthesis of π-Conjugated Poly(cycloborazane)s by Organometallic Polycondensation. Macromolecules 2000, 33, 8146–8148. [CrossRef]

127. Jia, W.-L.; Song, D.; Wang, S. Blue Luminescent Three-Coordinate Organoboron Compounds with a 2,2′-Dipyridylamino Functional Group. J. Org. Chem. 2003, 68, 701. [CrossRef]

128. Qi, Y.; Jäkle, F. Synthesis and Characterization of Organoboron Quinolate Polymers with Tunable Luminescence Properties. Macromolecules 2006, 39, 9041–9048. [CrossRef]

129. Nagata, Y.; Chujo, Y. Synthesis of Methyl-Substituted Main-Chain-Type Organoboron Quinolate Polymers and Their Emission Color Tuning. Macromolecules 2008, 41, 2809–2813. [CrossRef]

130. Nagata, Y.; Chujo, Y. Main-Chain-Type N,N′-Chelate Organoboron Aminoquinolate Polymers: Synthesis, Luminescence, and Energy Transfer Behavior. Macromolecules 2008, 41, 3488–3492. [CrossRef]

131. Reitzenstein, D.; Lammert, C. Localized versus Backbone Fluorescence in N-p-(Diarylboronyl)phenyl-Substituted 2,7- and 3,6-Linked Polycarbazoles. Macromolecules 2009, 42, 773–782. [CrossRef]

132. Hudson, Z.M.; Wang, S. Impact of Donor Acceptor Geometry and Metal Chelation on Photophysical Properties and Applications of Triarylboranes. Acc. Chem. Res. 2009, 42, 1584–1596. [CrossRef]

133. Li, H.; Jäkle, F. Facile Route to Organoboron Quinolate Polymers through Boron-Induced Ether Cleavage. Macromolecules 2009, 42, 3448–3452. [CrossRef]

134. Lorbach, A.; Bolte, M.; Li, H.; Lerner, H.-W.; Holthausen, M.C.; Ja¨kke, F.; Wargner, M. 9,10-Dihydro-9,10-diboranaanthracene: Supramolecular Structure and Use as a Building Block for Luminescent Conjugated Polymers. Angew. Chem. Int. Ed. 2009, 48, 4584. [CrossRef]

135. Lam, S.-T.; Zhu, N.; Yam, V.W.W. Synthesis and Characterization of Luminescent Rhenium(I) Tricarbonyl Diimine Complexes with a Triarylboron Moiety and the Study of Their Fluoride Ion-Binding Properties. Inorg. Chem. 2009, 48, 9664. [CrossRef]