

## Boron Difluoride Complex Dyes: Synthesis and Photophysical Properties

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**B**ORON difluoride ( $\text{BF}_2$ ) complex dyes are relatively non-polar and electrically neutral tending to reduce the perturbation of the conjugate functional characteristics. Consequently, they are frequently the favored choice for biological labeling. Also, their conjugates of low molecular weight structures are more likely to be permeable to live cells than other conjugates of charged chromophores. As a result of their high extinction coefficient, another significant application of boron difluoride complexes is their reactivity and high detection ability to volatile amine reagents accessible for HPLC and electrophoresis. They are more useful than the majority of other dyes with long absorption wavelength.  $\text{BF}_2$  complex conjugates are extremely valuable reagents for many bio-analytical screening purposes, such as their affinity to quench the fluorescence upon conjugation to certain biopolymers. In this review, we discuss the preparation of boron difluoride carbonyl based-complexes, including O-O double-dentate and N-O double-dentate dyes, as well as shedding light on their photophysical properties.

**Keywords:** Boron Difluoride; Complex Dyes; Synthesis; photophysical properties.

### Introduction

Functional dyestuffs, such as organic boron difluoride complexes, have been useful for hi-tech applications such as electronics, liquid crystalline displays, sensors, electrophotography, energy storage tools, security printing, optical data storage, organic light emitting devices, light control, solar cells and photodynamic therapy [1-11]. Functional dyestuffs are colorants that introduce a new function upon exposure to a small quantity of external energy, such as temperature, light, and magnetic/electric field. This external energy can control the electron-conjugated system leading to UV-Vis and/or emission changes, such as color change [12-24]. The chemistry of organic boron difluoride complexes has been recently received much more attention because of its significance for various practical applications [25]. Organic boron difluoride materials are recognized as fluorescent molecules with high quantum yields and high fluorescence intensity [25]. Hence, they have been extensively used in various applications, such as photo-dynamic cancer cure,

laser dyes, biological fluoro-probes, fluorescent indicators and photo-sensitizers. There are three main classes of organic boron difluoride ligands, including N-N double-dentate, N-O double-dentate and O-O double-dentate ligands as shown in **Figure 1** [22]. For the first two classes of boron difluoride complexes, both boradipyromethene (BODIPY) and 1,3,2-dioxaborine are their corresponding representatives [26, 27]. Moreover, BODIPY based  $\text{BF}_2$  complexes have been investigated extensively because of their excellent fluorescence properties. However, there are low number of reports on  $\text{BF}_2$  complexes with O-O double-dentate ligands, although the dioxaborine complexes have interesting fluorescence emission, first and second order non-linear optical properties, ion sensing ability, and can function as electron transport in organic emitting devices [28, 29]. In the relationship study between structure and photochemical properties; some reports demonstrated that annelation of electron donor to the dioxaborine ring resulted in improved absorption and fluorescence of the produced dyes and better resistance to hydrolysis [22, 25, 30].

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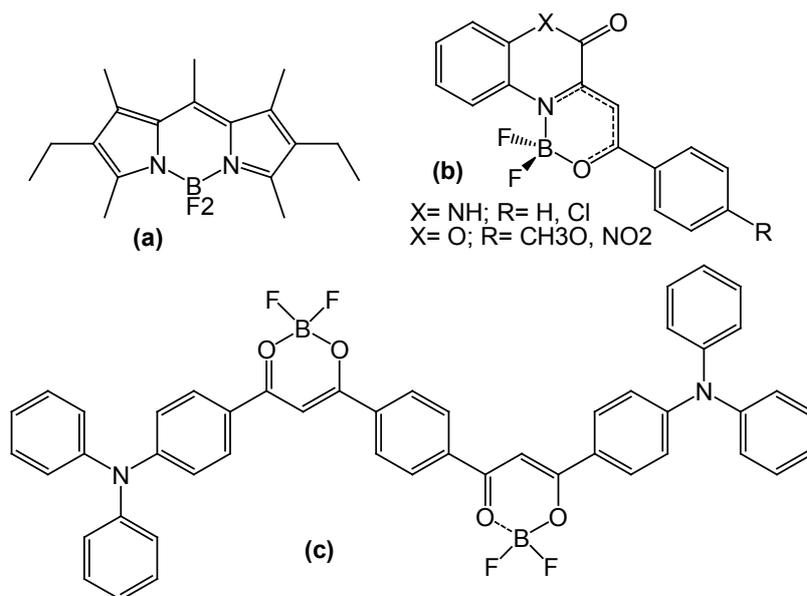


Fig. 1. Main classes of organic boron difluoride dyes depending on their ligand structure, including N-N double-dentate (a), N-O double-dentate (b) and O-O double dentate (c) ligands.

The boron difluoride complex fluorophores comprise spectral properties that are frequently better than those of fluorescein, tetramethylrhodamine and other dyes with longer absorption wavelength. Boron difluoride complex dyes are generally used to produce fluorescent conjugates of different natural and biological polymers as well as the production of other fluorescent products, such as enzyme substrates, phospholipids and polystyrene microspheres [22-30].

#### *BF<sub>2</sub> dyes containing O-O double-dentate ligands*

A series of rigid  $\beta$ -diketone boron difluoride complexes have been prepared and used as good organo-gelators in some mixed solvents. The balanced  $\pi$ - $\pi$  interactions which can be tuned as a result of molecular conjugation, are the major key to the gel formation from rigid  $\pi$ -conjugated organic structures lacking alkyl chains and

H-bonding units. This approach offers a new perspective in designing new rigid organogelator systems and expanding the gel-phase material with attractive photonic and electronic utilities [30]. Self-assembly studies have been carried out on BF<sub>2</sub>-substituted O-O double-dentate derivatives showing spontaneous absorption and well-assembled two-dimensional lamellae. The H-bond among the hydrogen on *ortho*-carbon of the phenyl moiety and BF<sub>2</sub> fluorine atom demonstrate a alongside configuration, while the H-bond among two carboxyl groups led to a pattern of molecules confronting each other. The outcomes have been noteworthy for designing and manufacturing various molecular assemblies of different molecular structures [31]. BF<sub>2</sub> complexes of styryl  $\beta$ -diketone derivatives have also been reported (Figure 5) [32].

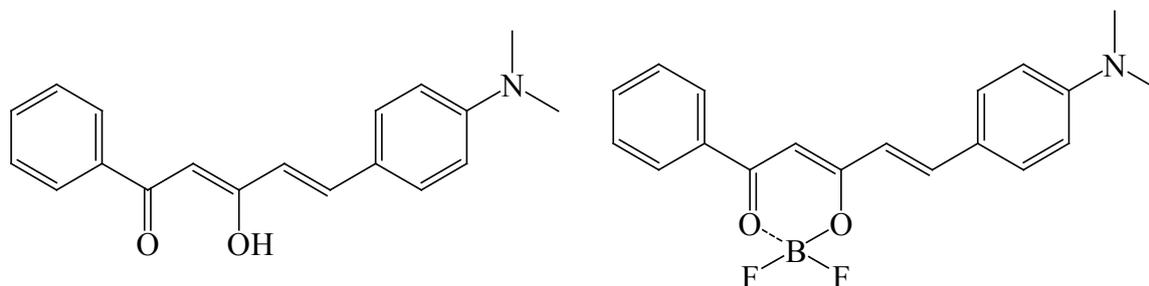


Fig. 2. BF<sub>2</sub> complex dyes with styryl  $\beta$ -diketone ligands.

Dissimilar arrangements of tetraketone that have been prepared as described in Figure 3, demonstrate an improved side by side intermolecular reaction because of the complex formation. The studies on the three dimensional crystal structures dedicate the nature of the intermolecular interactions due to H-bond formation. These intermolecular interactions are a significant feature fabricated by self-assembly [33].

Nanofibrils with a strong red emission produced from triphenylamine functionalized  $\beta$ -diketone- $\text{BF}_2$  complexes. The emission of the nanofibrillated films can be quenched effectively and quickly when exposed to the vapors of organic amines (Figure 4), such as triethylamine, cyclohexylamine and butylamine. However, no emission quenching was detected for other

ordinary reagents, such as dichloromethane, ethanol and toluene. The reported responsive time of these produced nanofibrillated films to aniline was about 1.06 s, which is considered as one of the most rapid fluorescence response to aniline [34]. The elevated sensitivity, and short life and decay-time of the triphenylamine functionalized  $\beta$ -diketone- $\text{BF}_2$  complexes for gaseous amines is due to the high surface area and large interspaces in the three dimensions network consisting of plenty of nanofibrils (prefer the improved adsorption and diffusion of amines vapors), as well as the improved emission quenching as a result of the improved intermolecular exciton diffusion alongside the long axis of one dimension nanostructures. The results were supportive to the design of new efficient fluorescence chemosensors in sensing traces of amines vapors [34].

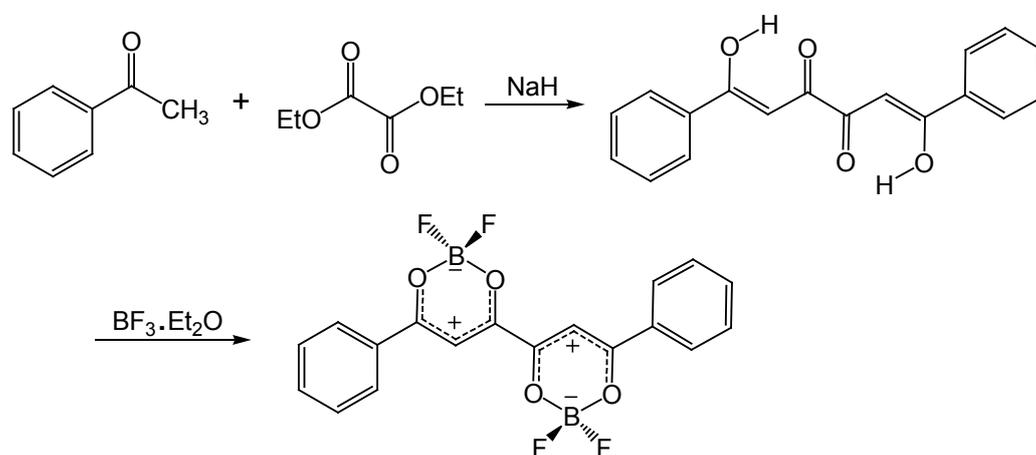


Fig. 3. Synthesis of tetraketone-based  $\text{BF}_2$  complex dye.

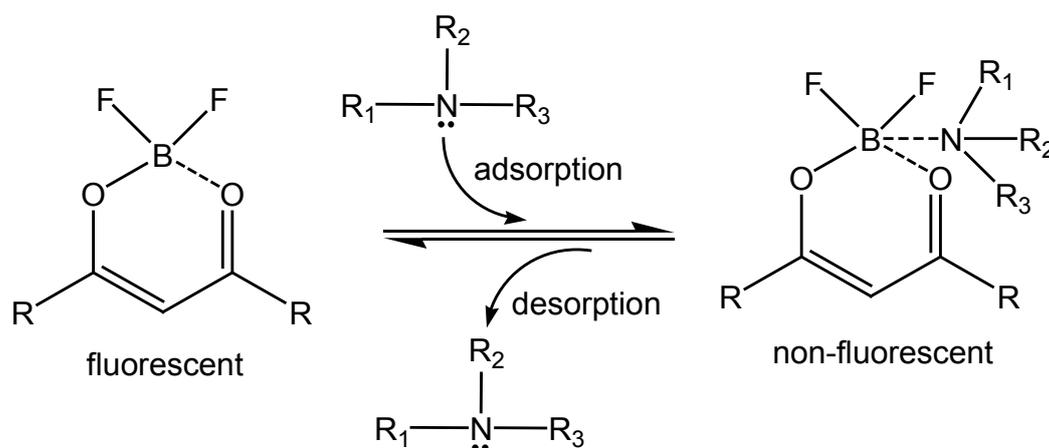


Fig. 4. Anticipated mechanism for the emission quenching upon exposure to volatile amines and its reversible process.

A number of novel boron difluoride polymethine chromophores with low fluorescence have been synthesized to afford exceedingly emissive open-chain products, which upon heating cyclization give pyridone chromophores with poor fluorescence (Figure 5) [35].

Bis(dioxaborine) carbazole derivatives have been synthesized, and low dimensional nano-structured films with diverse morphologies have been constructed using carbon chains. These obtained nano-structured films afforded strong fluorescence displaying the ability to function as fluorescent chemo-sensors for monitoring aniline fumes, with dissimilar responsive rates

and dissimilar sensitivity depending on their morphological properties that offer a large surface area for improved adsorption of vaporized molecules and allow expedient diffusion of that vaporized analytes (Figure 6) [36].

Bis(dioxaborine) fluorenes (Figure 7) have been reported as potential substrates for organic light-emitting diode (OLED) purposes [37]. There are various types of aromatic and heteroaromatic  $\text{BF}_2$  fluorophores bearing 1,3-diketone ligands have been reported as novel materials for light-emitting devices. Herein, the  $\text{BF}_2$ -chelating fragments behaved as electron-accepting groups. The trifluoromethyl group introduced into the

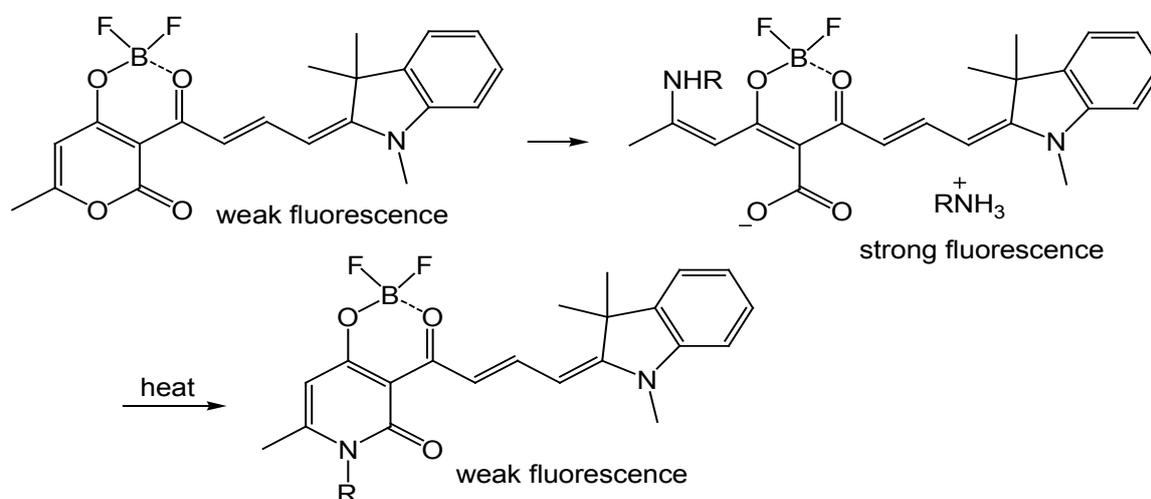


Fig. 5. Boron difluoride polymethine chromophore with low fluorescence with the ability to afford highly emissive open-chain chromophore, which upon heating cyclize to give pyridone with poor fluorescence.

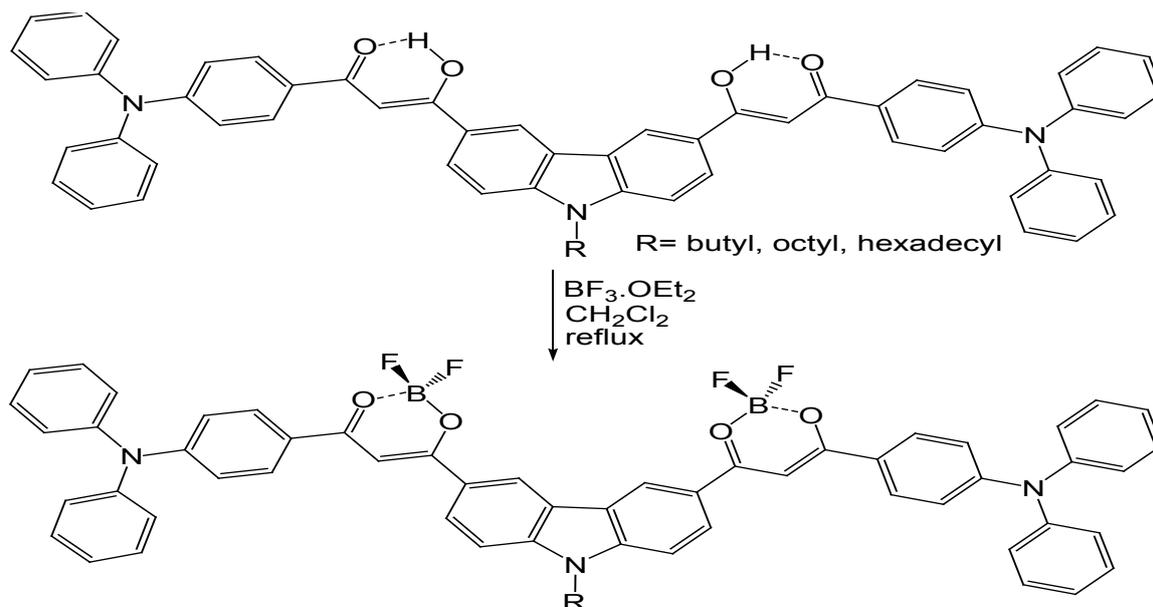


Fig. 6. Synthesis of bis(dioxaborine) carbazole complex dyes.

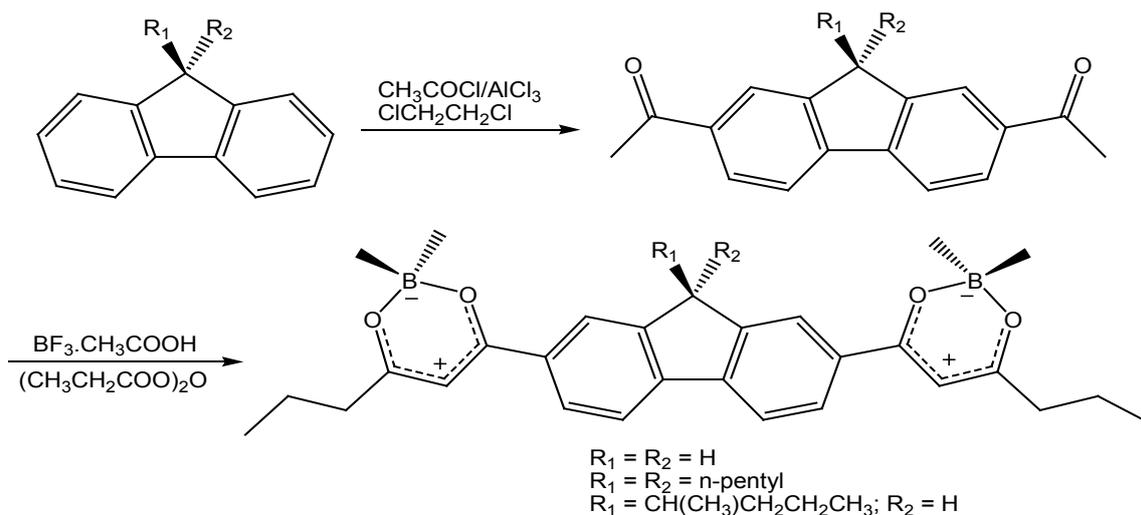


Fig. 7. Synthesis of bis(dioxaborine) fluorenes.

$BF_2$ -chelating fragment to amplify the electron affinity. The anion state of the produced  $BF_2$  complexes were stabilized as a result of the 1,3-diaryl-1,3-diketone ligands [38].

Doubly bridged boron difluoride complexes (Figure 8) with oxalyl-tethered pyrrole ligands have been reported to afford bright orange chromophores acting as a well discriminating chromogenic sensor for both fluoride and cyanide ions. Adding fluoride and cyanide ions into polar organic solvents containing doubly bridged boron difluoride complex dye, led to a reversible detachment of the  $BF_2$  bridges affording sharp variations in color [39, 40].

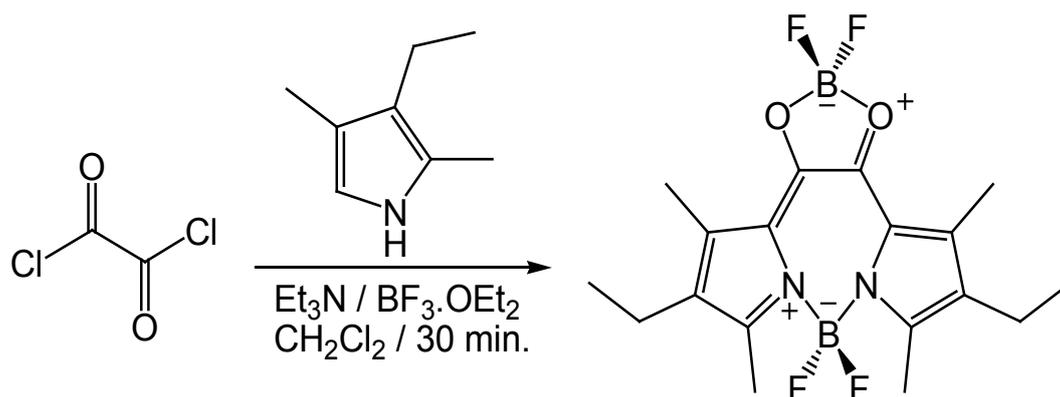
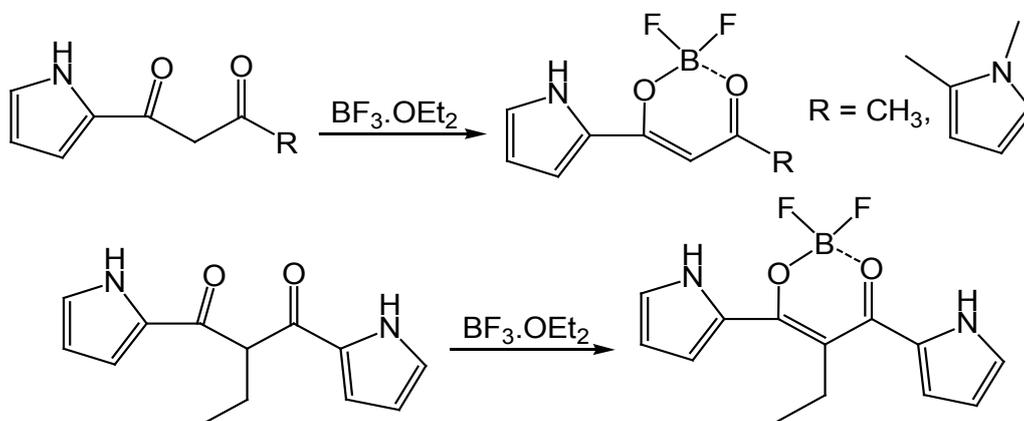
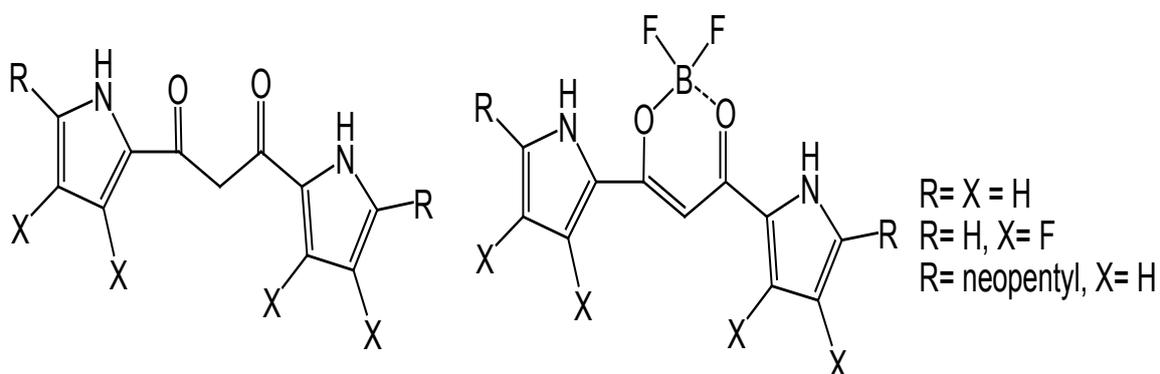
A supramolecular organogelators with  $\pi$ -conjugated binding sites have been prepared as anion responsive  $BF_2$  complex dyes of dipyrrolyldiketones or known as 1,3-dipyrrolyl-1,3-propanedione boron complexes to function as competent acyclic anion responsive materials through the inversion of pyrrole moieties [41]. The anion binding behavior was controlled by modifying the periphery of the receptors to afford supramolecular organogelators based on  $\pi$ - $\pi$  and van-der-waals interactions [42, 43]. The synthesis of  $BF_2$  complex derivatives starting from pyrrolyldiketones is described in Figure 9.

Another class of anion responsive materials based on  $BF_2$ -based complexes of 1,3-dipyrrolyl-1,3-propanedione fluorinated derivatives (Figure 10), have been reported as effectively binding anions. Hence, more modification in the acyclic receptor will recognize the binding and transporting of such biotic anion species, including proteins and

nucleotides, in water [44-46].  $BF_2$  complexes of 3-acyl tetramic acid derivatives was prepared by the acylation of pyrrolidine-2,4-diones with acid chlorides and  $BF_3$ -etherate [47].

Solutions of alkyl-substituted  $BF_2$  complexes have a green fluorescein-like fluorescence. Nevertheless, substituents that produce extra conjugation can shift the absorption and emission spectra to considerably longer wavelengths. Two dialkylaminogroups on the coumarin core complex to 2, 2-difluoro-1,3,2-dioxaborine moiety remarkably decreased the electron withdrawing capacity of the dioxaborine fragment. As a consequence, the spectral luminescent characteristics changed in going from a diethylamino group to a dipyrrolylino group. This alteration in the dye construction also led to considerably amplified resistance to hydrolysis [48]. 2-Aminochromones was also prepared by reacting phosgene iminium salts with 2'-hydroxyacetophenone- $BF_2$  complexes to afford  $\beta$ -chlorovinyllogous amide  $BF_2$  complex derivatives [49].  $BF_2$  complexes based on perylene and tetracene (Figure 11) ligands were prepared as novel category of electron deficient arenes with long wavelength absorption and better electron affinity because of the quadrupolar structures corresponding to the resonance contributors. Tetracene-based  $BF_2$  complexes are *n*-type semiconductor [50].

A boron difluoride complex containing dihydroxydione of octafluorotetracene fragment was reported as a novel class of electron accepting materials revealing long wavelength absorption depending on the perfluorotetracene

Fig. 8. Synthesis of doubly bridged  $\text{BF}_2$  complex.Fig. 9. Synthesis of  $\text{BF}_2$  complex derivatives from pyrrolyldiketones.Fig. 10. Dipyrrolyldiketone derivatives and their  $\text{BF}_2$  complexes.

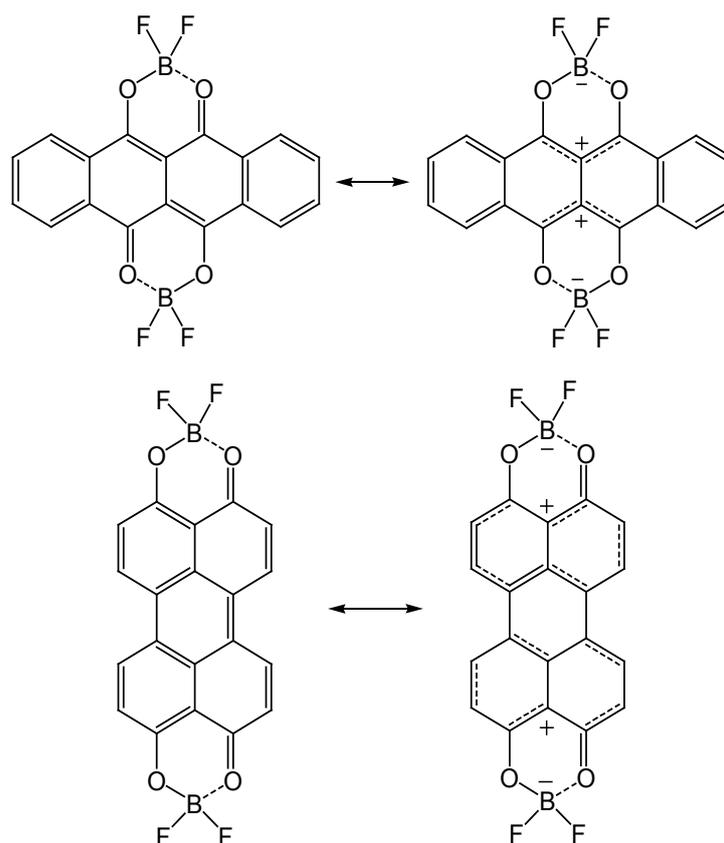


Fig. 11. Molecular structures of perylene and tetracene BF<sub>2</sub> complex dyes.

frame and elevated electron affinities owing to its quadrupolar configuration improved by fluorination [51]. Another novel boron difluoride complexes functionalized with a pyrene ligand have been reported as binuclear boron difluoride complexes for OLED. In the solid-state, they displayed strong red fluorescence. Compared to conventional emission and electron transport materials, additional structural optimization improving the emission intensity in the solid state is likely to afford more efficient emission materials [35]. Reacting BF<sub>3</sub>-etherate with 3-acetyl-4-hydroxy-1-methyl-2-quinolone (Figure 12) afforded the corresponding BF<sub>2</sub> complex which was subjected to a condensation reaction with a range of carbonyl compounds to produce polymethine and styryl 2-quinolone derivatives having efficient fluorescence and intense absorption in the visible region of the electromagnetic radiation. The formed BF<sub>2</sub> complex substantially enhances the reactivity of the methyl group of the acetyl fragment [52].

Boron difluoride O-O double-dentate complexes with a push-pull structural design, in

which a pyrazoline-1,3-dione is the electron donor; have been prepared. These new type of pyrazoline-1,3-dione based-complexes demonstrated photophysical properties that are extremely reliant to the solvent polarity and aggregation conditions. The molecular assembly of the crystal structure resulted in physically powerful charge transfer characterized with an extended excited state lifetime [53]. Reacting those 2-formyl ketone-based boron difluoride complexes with organometallic reagents has been reported to comprise an efficient preparation of 2-alkylidene ketones. Reacting Grignard reagents with 2-formyl ketones was revealed to be an efficient process for the preparation of 2-alkylidene ketones [54]. Chemoselective reaction of organolithium reagents with a boron difluoride complex of 3-oxopropanoates has been reported as shown in Figure 13. This attitude permits straightforward synthesis of different 1,3-dioxo-boron difluoride complexes and consequently led to the creation of asymmetrically substituted 1,3-diketones from their corresponding 3-oxopropanoate derivatives [55, 56].

*BF<sub>2</sub> dyes containing N-O double-dentate ligands*

It has been reported the preparation and X-ray crystallography of BF<sub>2</sub> complex from N-O double-dentate ligands originated from Schiff's bases of salicylaldehyde. However, its low emission intensity and quantum yield forced researchers to investigate for further methods toward such complex materials. 1,3-Enaminoketone derivatives are iso-steric analogues to the corresponding 1,3-enolic ketones, and are outstanding entrants as N-O double-dentate ligands to produce 1,3,2-oxazaborines, which are believed to exhibit photophysical characteristics comparable to those of 1,3,2-dioxaborines derived from 1,3-diketones [57]. New types of fluorescent dyes based on 2-ketopyrrole BF<sub>2</sub> Complexes have been synthesized. BODIPY dyes are precious molecular labels due to their intense fluorescence characteristics. The aryl substituted complexes N-O double-dentate ligands are fluorescent compounds that tend to emit at lower wavelengths than the analogous BODIPY dyes; N-N double-dentate ligands. These aryl substituted N-O double-

dentate complexes have a reduced fluorescence thus demonstrating the significance of the added, constrained, aromatic moiety in these structures [58]. New BF<sub>2</sub> complexes of 3-methylthio-enaminones have been prepared efficiently by the reaction of 3-methylthio-enaminones with BF<sub>3</sub>·Et<sub>2</sub>O in the existence of Et<sub>3</sub>N (Figure 14). These new materials are supportive for better understanding of chemical reactivity of enaminones and might be significant in pharmaceutical and agrochemical purposes [59].

Two types of new boron difluoride complexes with arylylidene-quinoxalin-2-ones or (arylylidene)-benzo[1,4]oxazin-2-ones as their heterocyclic 1,3-enaminoketones (Figure 15). The chelation process can be achieved readily and efficiently to give the targeted complexes in high yields. For those boron difluoride complexes, the large span red-shifts of UV-Vis absorption and intense emission originated from the substantial conjugated systems among the aromatic cycles and the chelating moieties [26].

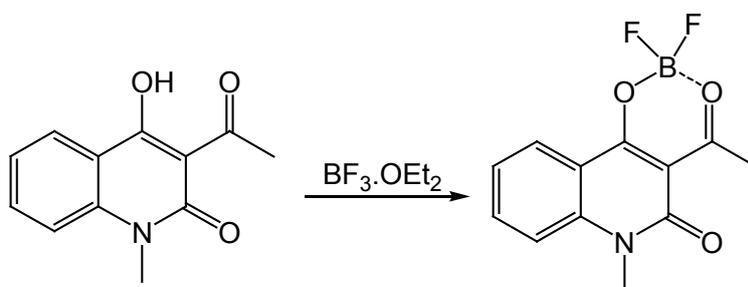


Fig. 12. Synthesis of 3-acetyl-4-hydroxy-1-methyl-2-quinolone BF<sub>2</sub> complex.

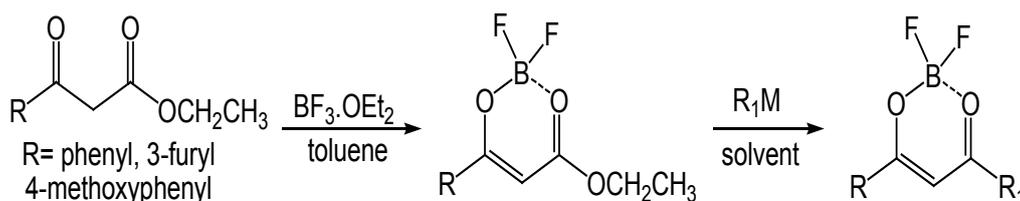


Fig. 13. Reaction of boron difluoride complexes of ethyl-3-oxopropanoates with organolithium reagent (R<sub>1</sub>M).

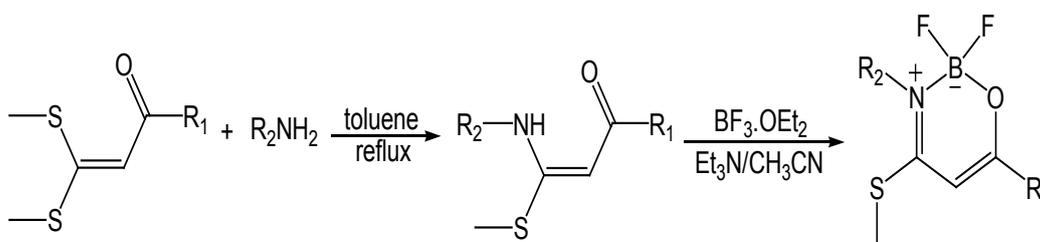


Fig. 14. Synthesis of BF<sub>2</sub> complex using 3-methylthio-enaminone.



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## أصباغ مركب البورون ثنائي فلوريد: طرق التحضير والخصائص الفيزيائية الضوئية

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أصباغ مركب البورون ثنائي فلوريد ( $BF_2$ ) غير قطبية نسبياً ومحايطة كهربائياً تميل إلى الحد من اضطراب الخصائص الوظيفية المترافقة. وبالتالي ، فهي في كثير من الأحيان الخيار المفضل لوضع العلامات البيولوجية. أيضاً ، من المرجح أن تكون اتحاداتهم ذات الهياكل الجزيئية منخفضة الوزن أكثر نفاذية للخلايا الحية من الاتحادات الأخرى للكرومفور المشحون. نتيجة لمعامل الانقراض المرتفع ، هناك تطبيق آخر مهم لمجمعات ثنائي فلوريد البورون هو تفاعله وقدرته العالية على الكشف عن الكواشف المتطايرة التي يمكن الوصول إليها لـ HPLC والرحلان الكهربائي. وهي أكثر فائدة من غالبية الأصباغ الأخرى ذات الطول الموجي الممتص. تعتبر اتحادات  $BF_2$  المعقدة كواشف قيمة للغاية للعديد من أعراض الفحص التحليلي الحيوي ، مثل تقاربها لإخماد الفلورة عند الاقتران ببعض البوليمرات الحيوية. في هذا البحث المراجعي ، نناقش تحضير مركبات البورون ثنائي فلوريد الكاربونيل ، بما في ذلك الأصباغ المزدوجة O-O و N-O ، وكذلك تسليط الضوء على خصائصها الفيزيائية الضوئية.