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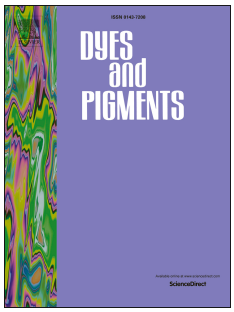

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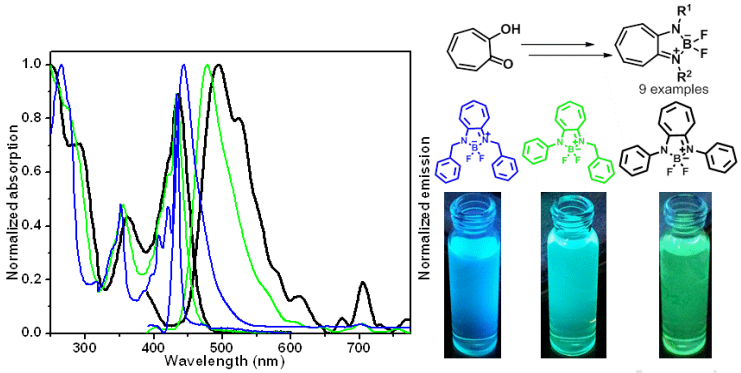

Novel Fluorophores: Syntheses and Photophysical Studies of Boron-Aminotroponimines

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Abstract: The syntheses and photophysical study of novel fluorescent boron-aminotroponimine complexes are described. The chemical structure of one of the boron complexes was confirmed by single crystal X-ray analysis, which shows the appearance of the distorted tetrahedral geometry at boron. The photophysical studies of these complexes revealed that the boron-aminotroponimines are fluorescent molecules with quantum yields ca. 0.17-0.28.

1. Introduction

Tropone and tropolone chemical moieties are unique seven-membered ring non-benzenoid aromatic system present in many biologically active natural products.[1] The electronic structure of the tropolonoids is distinctive from the benzenoid aromatic compounds and have characteristic photophysical properties (absorption and emission).[2, 4a-d] However, notable fluorescence was observed with the bioactive tropolonoid natural product colchicine, comprising a methoxytropone moiety, which has shown fluorescence after binding with the tubulin protein.[3] Later, fluorescent properties of tropolone were also explored, quantum yields of both tropolone and colchicine are very low at room temperature.[4] Moreover, substituted tropolone derivatives have shown fluorescence with enhanced quantum yields.[5-6]

Aminotroponimines (**Figure 1A**) are the synthetic aza-derivatives of tropolone, which are bidentate nitrogen chelating ligands.[7a] The aminotroponimine metal complexes are synthesized extensively and a few have been used as catalysts in selective organic transformation reactions.[7,12] Additionally, the synthesis of tropocoronands has also been elaborated, which are derived from cyclic aminotroponimines and metals.[8] However, the synthesis and hydrolytic stability of a few 2-bora-l,3-diazaazulene complexes have been reported in early 1962 but the fluorescent properties of these molecules are not explored so far.[9] On the other hand, Boron-Dipyrromethene (BODIPY, **Figure 1B**) fluorescent dyes are widely explored.[11] Importantly, organic fluorescent dyes are enormously useful in different fields for many applications such as labeling agents,[10a] chemical sensors,[10b,c] cell imaging agents[10d] and energy related cassette entities.[10fg]

Overall, fluorescent molecules consisting of tropolonoid core structure are yet to be fully explored. Hence, it is important to develop the fluorescent molecules containing tropolonoid aromatic system.

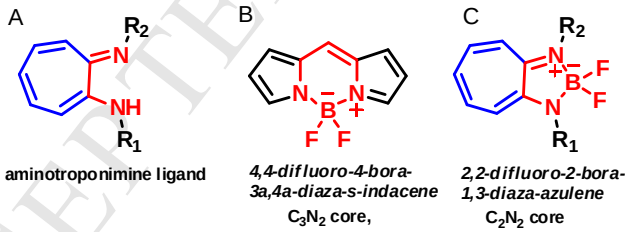


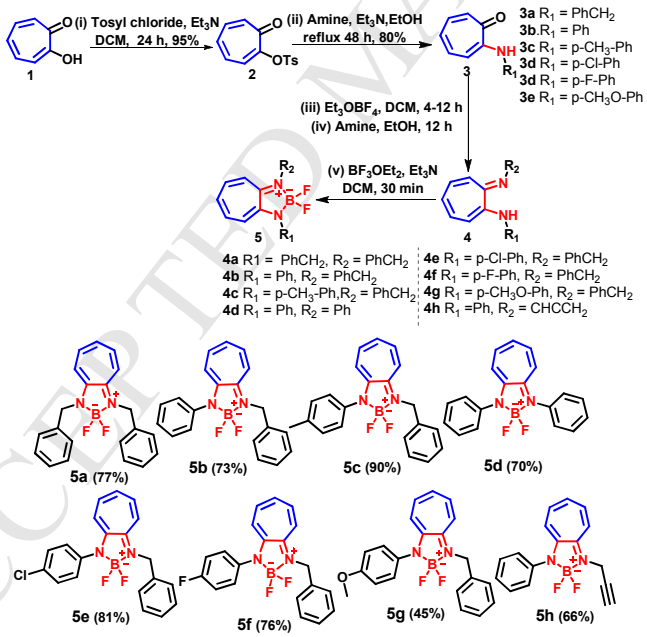
Figure. 1 Chemical structures of A) aminotroponimine ligand. B) boron dipyrromethene core. C) boron-aminotroponimine core (this work).

The fluorescent properties of a few reported tropolonoids and boron-dipyrromethene complexes inspired us to design a set of novel organic fluorescent molecules, boron-aminotroponimines (**Figure 1C**). These molecules are synthesized from aminotroponimine ligand, containing tropolonoid aromatic system, in place of dipyrromethene ligand of BODIPY complexes. However, boron-aminotroponimine core structure is a bicyclic core structure with the seven membered troponyl ring and a five membered ring, which is

distinctive from BODIPY core structure. Herein, we report the syntheses of various boron-aminotroponimines and examine their photophysical properties.

2. Results and Discussion

Syntheses and characterization: We began the syntheses of boron-aminotroponimine complexes from commercially available tropolone by following the previously reported procedures.[13] In scheme 1, tropolone was converted into 2-tosyloxytropone and then treated with different amines (ca. 3.0 equivalents) which produced *N*-substituted aminotropone derivatives (**3**) in good yield. These aminotropones (**3**) were further converted into aminotroponimines (**4**) by treating sequentially with triethyloxonium tetrafluoroborate and an amine.[11a]

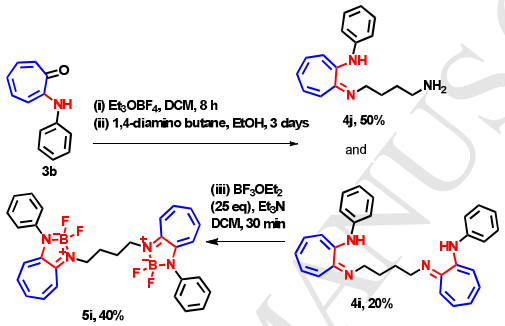


Scheme 1. Synthesis of boron-aminotroponimine complexes

Importantly, the reaction was fast with alkyl amines (benzyl/propergyl) as compared to aryl amines. The reported conversion of *N*-phenyl aminotropone (**3b**) into *N-(Phenyl)-2-(phenylamino)troponimine* (**4d**) was extremely slow (ca. 8.0 days) and yield was approx. 45.0%.[13a] Further, these aminotroponimines were converted into boron-aminotroponimines

by treating with an excess of boron trifluoride diethyl etherate (10 *equiv*.) and triethylamine (10 *equiv*.) at room temperature within 30.0 minutes. Exceptionally, the synthesis of *N,N'*-diaryl substituted boron complex (**5d**) required 20 equivalents of boron trifluoride diethyl etherate and triethylamine.

Further, we designed a dimeric complex **5i** that contain two monomeric units of **3b** connected by a butyl chain. This dimeric complex (**5i**) was synthesized from the *N*-phenyl aminotropone **(3b)** and 1,4-diaminobutane (**Scheme 2**).



Scheme. 2 Synthesis of dimeric aminotroponimine **4i** and its boron complex **5i.**

First *N*-phenyl aminotropone (**3b**) was treated with triethyloxonium tetrafluoroborate followed by the treatment with 1,4-diaminobutane results in formation of *N,N'-(diphenyl)-2-(1,4-diaminobutyl) ditroponimine* with moderate yield (20%). To avoid the formation of monomeric ligand (**4j**), only1.0 equivalent of 1,4-diaminobutane was added portionwise, but still we were unable to control the formation of the monomeric ligand (**4j**). Next, this dimeric ligand was subjected to BF_2-complexation under the above optimized conditions, which produced the desired complex (**5i**) with good yield (40.0%). The synthesized boron-aminotropnimine complexes are stable at room temperature/in the open air and were characterized by ^{1}H, ^{13}C, ^{11}B, ^{19}F NMR and HRMS (ESI-MS). Their spectral data are provided in the Supplementary Data.

Finally, the chemical structure of one of the boron complexes **5c,** was established by the single crystal X-ray analysis and its ORTEP diagram is depicted in **Figure 2A**.

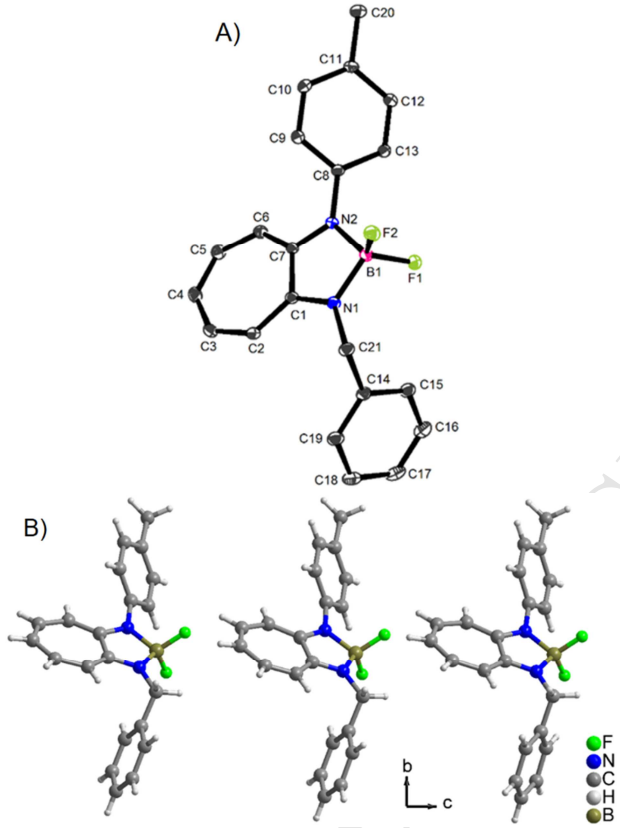


Figure. 2 A) ORTEP diagram of **5c** with 25% probability of ellipsoids, hydrogen atoms are deleted for clarity; B) Asymmetric unit of **5c**.

The X-ray analytical data as cif file is also deposited in Cambridge Crystallographic Data Center (CCDC) with CCDC number1400815. The asymmetric unit of complex **5c** is depicted in **Figure 2B,** which shows well-ordered molecular packing in its unit cell. The crystal structure analysis revealed that the boron center exists in distorted tetrahedral geometry and both the seven and five membered rings of boron-aminotroponimine core structure are tilted in 7.19^0. N_2-B bond is a typical N-B single bond, with the bond length 1.542 Å. The bond length of N_1-B is 1.528 Å, which is lesser than N_2-B bond length.[15] Selected bond lengths and bond angles are given in Table 1.

The crystals of the boron complex **5c** were grown in chloroform by slow evaporation method for single crystal X-ray diffraction studies. Though, we attempted to crystallize the other

solid boron complexes like **5a**, **5d** but our trials ended with needle like structures, from which we could not collect good X-ray diffraction data.

Table 1. Selected bond lengths and bond angles of boron complex **5c** in solid state.

selected bond lengths	selected bond angles	selected bond angles
C_1-C_7 = 1.463Å	N_1-B-N_2 = 98.10˚	F_1-B-N_2 = 113.90˚
C_1-N_1 = 1.334Å	F_2-B-N_2 = 112.26˚	C_1-N_1-B =112.87˚
C_7-N_2 = 1.350 Å	F_1-B-F_2 = 107.72˚	C_7-N_2-B = 111.64˚
N_1-B = 1.528 Å	F_2-B-N_1 = 113.44˚	N_2-C_7-C_1 =108.45˚
N_2-B = 1.542 Å	F_1-B-N_1 = 111.36˚	N_1-C_1-C_7 = 108.61˚

***Photophysical Studies*:** After synthesis, we performed the photophysical studies with the boron-aminotroponimine complexes (**5a-i**). First, the absorption and emission of aminotroponimine ligands (**4a-g**) were recorded in cyclohexane as control experiments. The absorption spectra of ligands (**4a-g**) in cyclohexane are depicted in **Figure 3A**, while their absorption spectra in acetonitrile are provided in SD (**Figure S2**). The UV-Vis spectrum of

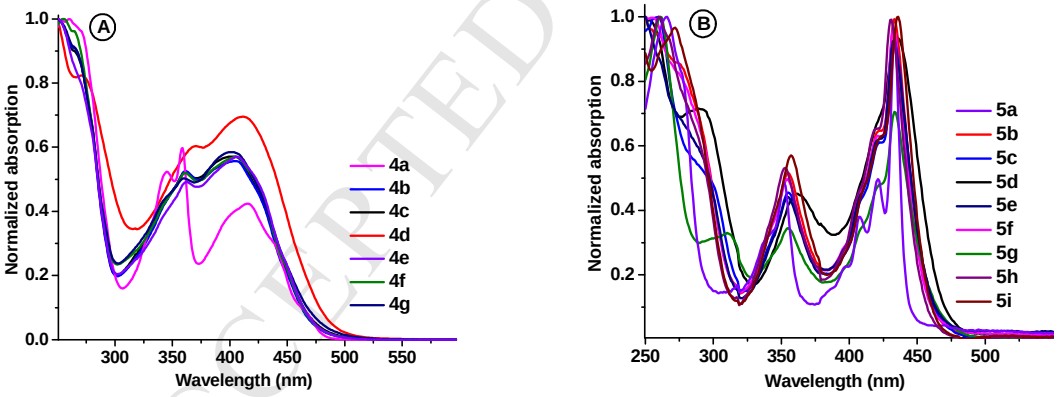


Figure 3. A) Absorption spectra of aminotroponiminate ligands (**4a-g**) in cyclohexane. B) Normalized absorption spectra of boron-complexes (**5a-i**) in cyclohexane, while their absoption spectra in acetonitrile provided in SD (Figure S2).

aminotroponimine ligand **4a** exhibits three peaks at 416 nm, 359 nm and 345 nm in cyclohexane. The absorption peaks at 359 and 345 nm has shown partial splitting and separated by 1130 cm^{-1}. While a clear separation was observed between the absorption peaks at 416 and 359 nm and separated by 3817.0 cm^{-1}. The absorption peak at 416 nm is a broad

absorption peak. The appearance of two major absorption peaks are due to transition to two different electronically excited states.[4a-d] The partial splitting between the two peaks at 359 nm and 345 nm is possibly due to the vibronic progression of the electronic transition to the same electronically excited state. In literature, similar kind of absorption patterns is reported for tropolone in cyclohexane.[4a-d] But, a redshift in absorption peaks and changes in their intensities are observed with aminotroponimine ligand **4a** when compared to tropolone absorption spectrum in cyclohexane. The absorption spectra of the remaining aminotroponimine ligands **4b-g** exhibits a broad absorption peak with the absorption maxima at ca. 402 (for **4d**, λ_{max}=412 nm) and a shoulder peak at 362 nm (**Figure. 3A**).

We also found a blueshift in absorption maxima for aminotroponimine ligands **4b/c/e/f/g** (λ_{max}=402 nm) over **4a** (λ_{max}=416 nm). This blueshift of ligands **4b/c/e/f/g** is due to replacing the benzyl substituent at amine nitrogen atom of the ligand with phenyl and substituted phenyl substituents. The presence of phenyl ring at *N*-atom of aminotroponimine decreases the basicity of nitrogen, and subsequently the delocalization of nitrogen lone pair decreases towards the troponyl ring. [14b,c] However, the substituents on the phenyl ring does not have any effect on the absorption maxima of ligands **4b/c/e/f/g**. For example, **4b/c/e/f/g** have shown similar absorption pattern though ligand **4e/f** contains 4-chlorophenyl/4-fluorophenyl substituents and ligands **4b/c/g** contains phenyl/4-methylphenyl/4-methoxyphenyl substituents on nitrogen atoms. In contrast, the absorption maxima of aminotroponimine ligand **4d** is redshifted over **4b/c/e/f/g** to ca. 412 nm with a shoulder peak at 362 nm. This is possibly occurring due to replacement of two benzyl substituents with the phenyl substituents, as a result extension of conjugation towards phenyl ring occurs through the imine *N*-atom of aminotroponimines.

All aminotroponimine ligands, other than **4a,** have shown broad absorption peak with absorption maxima at 402 nm and 412 nm (**4d**) and a shoulder peak at 362 nm. The

absorption spectra of aminotroponimine ligands (**4b-g**) in acetonitrile has shown more separation between 363 nm and 405-410 nm absorption peaks (SD, **Figure S2**), unlike absorption spectra in cyclohexane. Interestingly, in case of ligand **4a**, partial merging of absorption peaks at 346 and 358 nm was observed in acetonitrile. These studies supports that the appearance of shoulder peak at ~362 nm is most probably due to another electronic transition.[14a-d] Overall, two electronic transitions were observed for all aminotroponimine ligands in cyclohexane and acetonitrile, and substituents on the nitrogen atoms of ligands have significant effect on their absorption properties. However, the emission spectra of these ligands (**4a-g**) did not exhibit any significant emission peaks. These studies supports the feature that the ligands are non-fluorescent molecules in cyclohexane solvent.

Then, the absorption and emission spectra of boron-aminotroponimine complexes (**5a-i**) were recorded in cyclohexane. Their spectra are provided in **Figure. 3B**. The absorption spectra of these boron-aminotroponimine complexes exhibits only two major absorption bands at ~350 nm and 430 nm, with absorption maxima at ~430 nm (approx.) in cyclohexane. The occurrence of two absorption peaks are due to two different electronic transitions. The separation between the two absorption peaks are more or less similar for all boron complexes. Significant redshift in the absorption maxima is observed from aminotroponimines to boron-aminotroponimines. The summary of UV-vis absorption data of boron-aminotroponimines (**5a-i)** are provided in **Table 2** (column 2). The extinction coefficients (ε) of **5a-i** are determined at $\lambda_{abs,max}$ 430 nm from the respective absorption spectra and their values are described in **Table 2** (column 3). Unlike aminotroponimine ligands, absorption maxima for all boron complexes **5a-i** are observed at ~430 nm. Importantly, sharp absorption peaks were observed in case of boron-aminotroponimines in cyclohexane, ethanol and acetonitrile.

The appearance of sharp absorption peaks indicates the rigidification of the structure after BF_2-complexation. The absorption spectra of boron complex **5a** in cyclohexane has shown sharp absorption peaks at 433, 421, and 408 nm and in case of other complexes (**5b-i**) these peaks were appeared as shoulder peaks. The appearance of these peaks are due to vibronic transition to the same electronically excited state. This was further supported by the absorption spectra in ethanol and acetonitrile, where these peaks are merged and single absorption peak was observed at ~425 nm (SD, **Figure S1/S2**). From the literature, it has been learnt that the occurrence of vibronics are indication of less conformational disorder.[14a] In case of boron complex **5a,** the occurrence of well-resolved vibronic peaks are possibly due to less conformational disorder. Whereas, in boron complex **5d** the vibronic peaks are merged and single absorption peak was observed, this is probably due to more conformational disorder.

The emission spectra of boron complexes (**5a-i**) were then recorded at excitation wavelength 350 nm in cyclohexane. These spectra are depicted in **Figure. 4B** and emission maxima ($\lambda_{em.}$), Stokes shifts and quantum yields are summarized in **Table 2**. Boron-aminotroponimines have shown remarkable fluorescence character. It is important to discuss the emission properties of these complexes. First of all, unlike absorption, tremendous variation in the emission properties of boron-aminotroponimines were observed. Nature of the substituents on the nitrogen atoms of the boron-aminotroponimines have dramatic effect on emission properties such as emission maxima and quantum yield. Boron complex **5a** exhibits strong emission at 445 nm (blue fluorescence) with 12 nm Stokes shift. Whereas the boron complexes **5b**/**5h**, containing one *N*-phenyl substituent at nitrogen atom, have shown emission maxima (λ_{em}) at 478 nm (green fluorescence) with larger Stokes shift (44 nm). Interestingly, complex **5d**, containing *N*,*N'*-diphenyl substituents on nitrogen atoms, emits at wavelength 487 nm (λ_{em}) with further enhancement in Stokes shift (59 nm). Thus, *N*-phenyl

substituted boron complexes shows noticeable redshift in their emission maxima with a corresponding increase in the Stokes shift. The emission maxima of boron complexes **5e/f** is more redshifted when compare to **5b** and their Stokes shifts are 50 and 47 nm, respectively (chlorophenyl/fluorophenyl substituents). Moreover, boron complexes **5c** has shown further redshift in emission maxima when compare to **5b/e/f**. Overall, presence phenyl and substituted phenyl substituents on nitrogen atoms of boron complexes leads to larger Stokes shifts. Furthermore, the electron donating groups containing phenyl substituents on nitrogen atom of boron complexes causes more redshift.

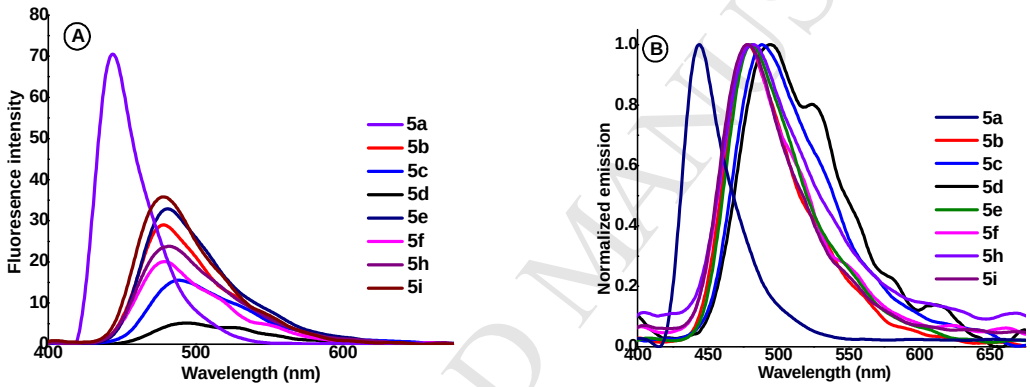


Figure 4. A) Emission spectra of boron-aminotroponimine complexes (**5a-i**) in cyclohexane at 20.0 μM concentration. B) Normalized emission spectra of boron complexes (**5a-i)** in cyclohexane.

Table 2. Photophysical parameters of *boron-aminotroponimines*

entry	$\lambda_{abs}{}^{a}$ (nm)	ε^{a} (M^{-1} cm^{-1})	$\lambda_{em}{}^{ac}$ (nm)	$\Phi_f{}^{b}$	Stokes shift (nm)	Stokes shift (cm^{-1})
5a	433, 421, 408, 352	36881	445	0.17	12	622
5b	434, 421, 355	16709	478	0.17	44	2120
5c	434, 421, 355	24651	487	0.07	53	2508
5d	435, 362	18342	494	0.05	59	2746
5e	432, 421, 355	12789	482	0.17	50	2402
5f	432, 421, 355	11571	479	0.15	47	2272
5g[a]	433, 355	15155	nd	nd	nd	nd
5h	431, 419, 354	16670	478	0.15	47	2281
5i	435, 421, 357	18042	478	0.28	43	2068

[a]All measurements were carried out in cyclohexane, [b]Quantum yields were determined by considering quinine sulfate in 0.1 M H_2SO_4 as standard reference. [c]λ_{ex} = 350 nm. [d]boron complex **5g** has shown negligible fluorescence in cyclohexane.

Here, we also attempted to investigate the effect of excitation wavelength on emission maxima. The boron complexes **5a**/**b**/**c**/**e**/**f** were excited at a wavelength 433 nm in cyclohexane. Their emission spectra are given in Supplementary Data. These results indicate that the emission wavelength is independent of excitation wavelength.

Further, the quantum yields of boron-aminotroponimines (**5a-i**) were determined in cyclohexane by following the well-known relative method.[16] Quinine sulfate in H_2SO_4 (0.1 M) was used as reference standard. All the measurements were carried out under same instrumental parameters (λ_{ex} = 350 nm, for reference and samples to be analyzed) and at 20 ^{o}C. The obtained emission spectra are depicted in **Figure. 4B** and their quantum yields are given in **Table 2.** As mentioned above, nature of the substituents on nitrogen atoms have significant effect on the quantum yield of boron-aminotroponimines **5a-i**. The maximum quantum yield achieved with the monomeric boron-aminotroponimines **5a**/**b**/**e/f/h** is 0.15-0.17 (Φ_f). The quantum yield of remaining monomeric boron-aminotroponimines such as **5c/d** is 0.07 and 0.05, respectively. However, as envisioned, the quantum yield of the dimeric boron complex **5i** was remarkably increased, almost twofold (Φ_f=0.28). Interestingly, the calculated quantum yield for boron complexes **5a** and **5b** was same irrespective of their substituents. In case of other complexes, we found that the presence of electron donating groups on *N*-atoms of their ligands such as 4-methylphenyl (**5c,** Φ_f=0.07), 4-methoxyphenyl (**5g,** negligible fluorescence) leads to dramatic decrease in the quantum yield, while presence of electron withdrawing substituents such as 4-chlorophenyl (**5e,** Φ_f=0.17) and 4-fluorophenyl (**5f,** Φ_f=0.15) does not lead to significant changes in quantum yield of respective boron complexes when compared to **5b (**Φ_f=0.17). Overall, substituents at the nitrogen atoms

of the boron-aminotroponimines have significant effect on emission maxima and quantum yield, unlike absorption.

We also recorded the absorption and emission spectra of boron-aminotroponimines (**5a-i**) in ethanol. Their spectra are provided in Supplementary Data. Unlike in cyclohexane, only two absorption peaks at ~425 and 350 nm are observed with all boron-aminotroponimines. However, the blue shifts (5-10 nm) in absorption and emission maxima was observed in ethanol and the larger Stokes shifts were also observed in ethanol. Except for **5a**, their quantum yields were significantly diminished in ethanol (**Table S3, SI**). Overall, our spectroscopic studies strongly suggest that boron-aminotroponimine complexes are fluorescent molecules like BODIPY analogue, but aminotroponimine precursors are non-fluorescent molecules.

3. Conclusions

In summary, we have successfully synthesized various boron-aminotroponimine complexes containing tropolonoid aromatic system and their initial photophysical properties are explored. The photophysical properties are demonstrated in two solvent systems. We also established the chemical structure of one of the boron-complex **5c** by single crystal X-ray analysis. Our initial studies revealed that only boron-aminotroponimine complexes are fluorescent molecules. No emission properties were observed with the aminotroponimine ligands. These observations provide enormous opportunities to construct novel fluorophores containing boron-aminotroponimine structure by tuning the chemical structure.

4. Experimental Section:

Materials, instrumentation and methods: All required materials and solvents were purchased from commercial suppliers and used without any further purification unless noted**.**

Anhydrous dichloromethane was freshly prepared by distilling over Calcium hydride. Reactions were monitored by thin layer chromatography, visualized by UV and Ninhydrin. Column chromatography was performed in 230-400 and 100-200 mesh silica. Mass spectra were obtained from Bruker micrOTOF-Q II Spectrometer and the samples were prepared in acetonitrile and injected in acetonitrile and water mixture. NMR spectra were recorded on Bruker AV-400 at room temperature (^{1}H: 400 MHz, ^{13}C: 100.6 MHz). ^{1}H and ^{13}C NMR chemical shifts were recorded in ppm, downfield from tetramethyl silane. Splitting patterns are abbreviated as: s, Singlet; d, doublet; dd, doublet of doublet; app d, apparent doublet; app dd, apparent doublet of doublet; t, triplet; q, quartet; dq, doublet of quartet; m, multiplet. FT-IR spectra were obtained from Bruker Tensor 27 spectrometer from 4000-600 cm^{-1}. Absorption spectra were obtained using Perkin-Elmaer λ-750. Fluorescence spectra were obtained from Perkin-Elmer LS-55 using Xenon lamp. All spectroscopic measurements were carried out with spectroscopic grade, non-degassed solvents and at 20 ^{o}C.

Relative fluorescence quantum yields were determined by comparing with quinine sulfate quantum yield in 0.1M H_2SO_4 (0.54). The obtained values were substituted in the equation given below.

$$\Phi_x = \Phi_r \times \frac{F_x}{F_r} \times \frac{1 - 10^{-A_r}}{1 - 10^{-A_x}} \times \frac{\eta_x^2}{\eta_x^2}$$

The subscripts *x* and *r* refers sample to be measured and reference. *F* denotes the area under curve of the integrated fluorescence spectra, *A* stands for optical density at excited wavelength, η represents refractive index of the solvent used.

General procedure for the synthesis of boron-aminotroponimines: 0.1 gm (0.33 mmol) of Aminotroponimine (**4a**) was dissolved in anhydrous dichloromethane (6 mL) and to this 10 equivalents (465 mL, 3.33 mmol) of anhydrous triethylamine was added under nitrogen

atmosphere. To the resultant reaction mixture 10 equivalents of $BF_3.OEt_2$ (411 mL, 3.33 mmol) was added dropwise and mixture left to stir at room temperature until reaction completion, as judged by TLC, all reactions were completed within half an hour (For the synthesis of **5d,** 20 equivalents of triethylamine and $BF_3.OEt_2$ was used, whereas for the synthesis of **5i,** 25 equivalents of triethylamine and $BF_3.OEt_2$ was used). All volatiles were evaporated under reduced pressure and to the crude residue, water was added to quench the unreacted $BF_3.OEt_2$ and extracted with ethyl acetate (thrice). The combined organic layers were dried over sodium sulfate and concentrated. The crude product was purified through silica gel column chromatography by using 100% DCM as the mobile phase. Boron complex **5a** was obtained in 77.0% yield. Remaining all boron complexes were synthesized by following this general procedure.

*Boron complex **5a**:* The pure product was obtained as light green solid. (90 mg, isolated yield = 77%, mp = 159-161 ^{o}C). FT-IR (KBr plate) ν = 2922, 1599, 1546, 1495, 1469, 1452, 1439, 1415, 1351, 1298, 1248, 1144, 1096, 1075, 1056, 995, 733, 698. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.6 Hz, 4H), 7.33 (t, *J* = 7.5 Hz, 4H), 7.26 – 7.21 (m, 4H), 6.81 – 6.65 (m, 3H), 4.85 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.60, 138.50, 136.77, 128.71, 127.23, 127.18, 122.92, 113.93, 46.85. ^{11}B NMR (128 MHz, $CDCl_3$) δ 5.57 (t, *J* = 30.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -138.32 (dd, *J* = 61.6, 30.5 Hz). HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd. for $C_{21}H_{19}BF_2N_2$ 349.1686, found 349.1723.

*Boron complex **5b**:* The pure compound was obtained as yellow thick liquid. (85 mg, isolated yield = 73%) FT-IR (KBr plate) ν = 2920, 2850, 1600, 1545, 1494, 1469, 1452, 1436, 1412, 1251, 1101, 1076. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (t, *J* = 7.7 Hz, 2H), 7.42 (d, *J* = 5.0 Hz, 4H), 7.37 - 7.29 (m, 4H), 7.27 - 7.24 (m, 2H), 7.02 (app d, *J* = 10.7 Hz, 1H), 6.84 - 6.76 (m, 2H), 4.86 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.55, 156.26, 139.05, 138.60, 138.55, 136.64, 129.68, 128.71, 127.27, 127.19, 126.15, 114.89, 114.70, 46.88. ^{11}B NMR (128 MHz,

$CDCl_3$) δ 5.41 (t, *J* 29.8). ^{19}F NMR (376 MHz, $CDCl_3$) δ -135.68 – -136.02 (m). HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd. for $C_{20}H_{17}BF_2N_2$ 335.1529, found 335.1546.

*Boron complex **5c**:* The pure product was obtained as yellow solid. . (100 mg, isolated yield = 90%, mp = 149-149 ^oC) FT-IR (KBr plate) ν = 2923, 2852, 1599, 1544, 1512, 1468, 1437, 1414, 1350, 1251, 1099, 1075, 1000, 727. ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.4 Hz, 2H), 7.38 – 7.22 (m, 9H), 7.03 (app d, *J* = 10.7 Hz, 1H), 6.82 - 6.75 (m, 2H), 4.86 (s, 2H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.63, 156.22, 138.52, 138.42, 137.02, 136.73, 136.32, 130.31, 128.70, 127.27, 127.25, 125.87, 123.79, 114.74, 114.63, 46.89, 21.13. ^{11}B NMR (128 MHz, $CDCl_3$) δ 5.37 (t, *J* 29.7). ^{19}F NMR (376 MHz, $CDCl_3$) δ -135.88 – -136.31 (m). HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd. for $C_{21}H_{19}BF_2N_2$ 371.1505, found 371.1540.

*Boron complex **5d**:* The pure product was obtained as yellow fine solid. (90 mg, isolated yield = 70%, mp = 165-167 ^oC) FT-IR (KBr plate) ν = 2919, 2850, 1592, 1542, 1493, 1474, 1453, 1434, 1405, 1250, 1097, 1060, 751, 694. ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.47 (m, 4H), 7.44 (d, *J* = 7.2 Hz, 4H), 7.38 - 7.30 (m, 4H), 7.10 (app d, *J* = 10.6 Hz, 2H), 6.87 (t, *J* = 9.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.24, 138.93, 138.64, 129.73, 127.30, 126.24, 125.07, 115.66. ^{11}B NMR (128 MHz, $CDCl_3$) δ 5.21 (t, *J* 28.7). ^{19}F NMR (376 MHz, $CDCl_3$) δ -133.38 (dd, *J* 57.4, 28.6). HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd. for $C_{19}H_{15}BF_2N_2$ 343.1192, found 343.1048.

*Boron complex **5e**:* The pure product is obtained as yellow viscous liquid. (75 mg, isolated yield = 81%) FT-IR (KBr plate) ν = 2923, 2852, 1600, 1544, 1492, 1468, 1452, 1436, 1415, 1251, 1100. ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.32 (m, 9H), 7.32 – 7.23 (m, 2H), 7.02 (app d, *J* = 10.7 Hz, 1H), 6.87 - 6.78 (m, 2H), 4.87 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.35, 147.07, 138.86, 138.70, 137.63, 136.43, 132.71, 129.85, 128.72, 127.48, 127.32, 127.21, 124.42, 115.33, 114.49, 46.88. ^{11}B NMR (128 MHz, $CDCl_3$) δ 5.32 (t, *J* = 29.8 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -135.49 – -135.93 (m). HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd. for $C_{20}H_{16}ClBF_2N_2$ 369.1139, found 369.1163.

*Boron complex **5f**:* The pure product is obtained as yellow viscous thick liquid. (70 mg, isolated yield = 76%) FT-IR (KBr plate) ν = 2920, 2850, 1641, 1600, 1545, 1508, 1469, 1438, 1253, 1229, 1213, 1102, 815, 796, 732, 706. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.36 (m, 4H), 7.36 – 7.30 (m, 3H), 7.31 – 7.23 (m, 2H), 7.22 – 7.14 (m, 2H), 6.96 (app d, *J* = 10.7 Hz, 1H), 6.87 - 6.79 (m, 2H), 4.86 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ162.77, 160.32, 156.63, 156.33, 138.75, 138.69, 136.53, 128.74, 127.97, 127.89, 127.33, 127.25, 124.17, 116.72, 116.49, 115.13,114.47, 46.91. ^{11}B NMR (128 MHz, $CDCl_3$) δ 5.33 (t, *J* = 29.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.59 (s), -135.93 (dd, *J* = 59.3, 29.3 Hz). HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd. for $C_{20}H_{16}BF_3N_2$ 353.1435, found 353.1437.

*Boron complex **5g**:* The pure product is obtained as yellow viscous thick liquid. (50 mg, isolated yield = 45%) FT-IR (KBr plate) ν = 2956, 2918, 2849, 1643, 1599, 1544, 1510, 1469, 1454, 1438, 1410, 1245, 1099. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.4 Hz, 2H), 7.38 – 7.30 (m, 4H), 7.30 – 7.22 (m, 3H), 7.05 – 6.97 (m, 3H), 6.78 (m, 2H), 4.86 (s, 2H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ158.62, 156.93, 156.12, 147.07, 138.52, 138.41, 136.75, 131.68, 130.90, 128.71, 127.28, 127.26, 127.22, 124.45, 123.96, 123.71, 114.96, 114.70, 114.57, 55.51, 46.91. ^{11}B NMR (128 MHz, $CDCl_3$) δ 5.32 (t, *J* = 29.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -136.24 (dd, *J* = 59.3, 29.4 Hz). HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd. for $C_{20}H_{16}BF_3N_2$ 387.1454, found 387.1473.

*Boron complex **5h**:* (80 mg, isolated yield = 66%) FT-IR (KBr plate) ν = 2923, 2852, 1600, 1545, 1492, 1463, 1412, 1252, 1154, 1102, 1051, 995, 735, 695. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 - 7.51 (m, 1H), 7.47 (t, *J* = 7.7 Hz, 3H), 7.41 – 7.29 (m, 4H), 7.16 (app d, *J* = 10.7 Hz, 1H), 7.04 (app d, *J* = 10.8 Hz, 1H), 6.91 (t, *J* = 9.7 Hz, 1H), 4.38 (s, 2H), 2.29 (t, *J* = 2.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.79, 155.53, 147.05, 138.99, 138.81, 138.74, 129.68,

127.30, 126.08, 124.60, 115.44, 114.63, 77.66, 72.04, 14.07. ^{11}B NMR (128 MHz, $CDCl_3$) δ 4.93 (t, *J* = 29.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -136.06 – -139.11 (m). HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd. for $C_{16}H_{13}BF_2N_2$ 283.1216, found 283.1204.

Boron complex ***5i****:* (30 mg, isolated yield = 40%) FT-IR (KBr plate) ν = 2923, 2852, 1599, 1544, 1492, 1468, 1453, 1436, 1415, 1251, 1101, 746, 701. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 - 7.45 (m, 6H), 7.38 - 7.33 (m, 6H), 7.31 – 7.22 (m, 3H), 7.04 (app d, *J* = 10.9 Hz, 2H), 6.95 (app d, *J* = 10.7 Hz, 2H), 6.83 (t, *J* = 9.6 Hz, 2H), 3.72 (s, 4H), 2.00 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.31, 156.11, 139.10, 138.62, 138.33, 129.66, 127.11, 126.22, 123.71, 113.99, 42.87, 25.94. ^{11}B NMR (128 MHz, $CDCl_3$) δ 5.22 (t, *J* = 30.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -136.37 (dd, *J* = 60.8, 30.0 Hz). HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd. for $C_{30}H_{28}B_2F_4N_4$ 565.2339, found 565.2302.

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Supplementary Data

Experimental procedure and characterization data of aminotroponimines and boron-aminotroponimines (^{1}H, ^{13}C, ^{11}B, ^{19}F NMR and HRMS) are provided in the Supplementary Data.

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Research Highlights

- The syntheses and characterization of monomeric and dimeric Boron-Aminotroponimines.
- Exploring the absorption and fluorescence properties of Boron-Aminotroponimines.
- Boron-Aminotroponimines core structure is distinctive from Boron-Dipyrromethenes.
- The fluorescence properties are tunable.