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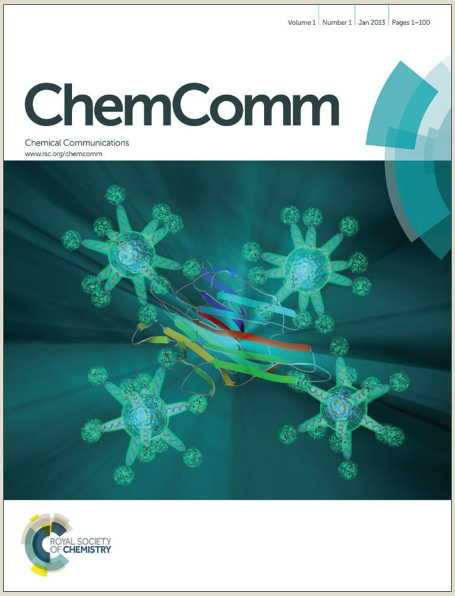

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Highly Emissive Organic Solids with Remarkably Broad Color Tunability Based on N, C-Chelate Four-Coordinate Organoborons

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Abstract. Molecular fluorophores based on N,C-chelate four-coordinate organoborons exhibit tunable solid-state emission colors that cover the whole visible region from blue to red. The emission color can be tuned through the substituents on either quinolines or on boron center.

Design and synthesis of luminescent organic materials is of fundamental importance because of their potential application in optoelectronic devices.[1] Such luminescent organic materials can also hold significant potential in the field of bio-imaging.[2] Therefore, the development of novel solid emitters[3] which do not casue aggregation-induced emission quenching[4] has emerged a hot topic of research. However, in most cases, the design is heavily relied on mere functionalization of existing fluorophores. Considering the demand of solid light emitters in material science and biology, there is an urgent need for the identification novel core structures, with full color-tunability, capable of emitting light in the aggregation state.[5]

In recent years, organoborons are considered as promising light emitting materials owing to their intense luminescence and high carrier mobility.[6] In addition to their application in material sciences, these compounds have potential applications in biology as a cell marker.[7] The most potential examples of fluorescent organoboron compounds are borondipyrromethene (BODIPY) dyes and its analogues.[8] However, in general, those dyes are emissive in dilute solutions and they become non-emissive in the aggregate state[9] with some exceptions.[10] Therefore, it is very challenging to develop highly emissive solid organoborons; especially with a full-color tunability using a single core skeleton by appropriate tuning of the substituents.

Over the years, several research group across the world have initiated programme on identifying a single type of boron-containing molecules capable of emitting light at different wavelengths. In 2005, Wang and coworkers identified the luminescent N,N-chelate boron complexes whose solid state emission can be tuned from blue to red.[11] In 2007, Yamaguchi and coworkers reported full-color tunable emissive organic solids based on 3-boryl-2,2’-bithiophene as a versatile core skeleton.[12] You and coworkers reported regiospecific N-heteroarylation of amidines for full-color-tunable boron difluoride dyes with mechanochromic luminescence.[13] Zhang and Wang reported construction of strongly emissive full-color tunable boron-containing materials by functionalizing a boron-chelate-ring-fused π-conjugated core.[14] Very recently, Tanaka and Chujo showed that the emission color in boron diiminates in the solid states can be modulated by the substituents.[15]

Inspired by the above reports, we designed a new class of full-color tunable solid light emitters based on N,C-chelate four-coordinate organoborons (Fig 1).[16] It was envisaged that the appropriate choice of substituent on either boron or on N,C-chelate might allow us to achieve color-tunability in the solid state that span the whole visible region. Herein, we report the successful implementation of our studies.

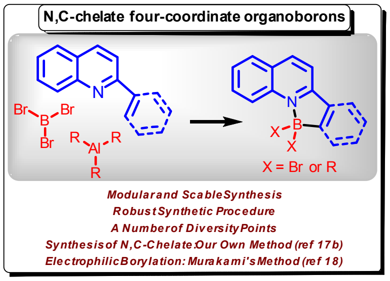

Figure 1. General design of N,C-chelate four-coordinate organoborons

A series requisite N,C-chelate four-coordinate organoborons were synthesized in a stepwise manner as outlined in Scheme 1. The pre-requisite 2-substituted quinolines were prepared by the method developed by us[17] with slight modifications. Treatment of 2-aminobenzaldehydes with appropriate alkynes under the catalysis

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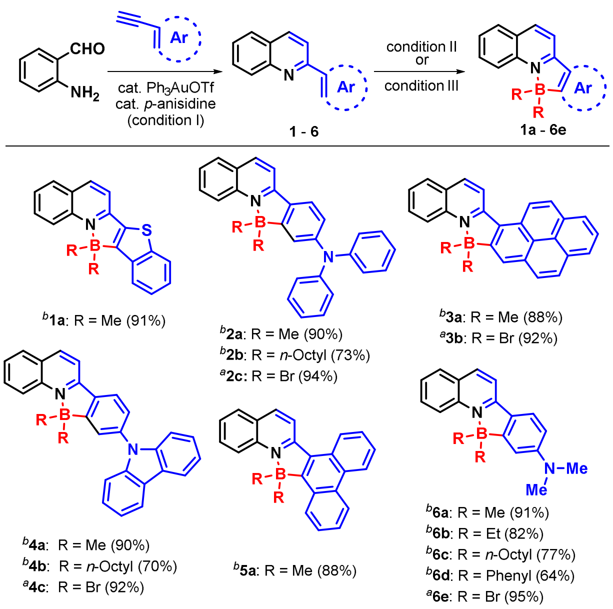
with Au(I) and *p*-anisidine provided the products **1-6** in yields ranging from 80-95%. Following the procedure reported by Murakami,[18] the targeted quinoline–borane complexes were synthesized from 2-arylquinolines through an electrophilic aromatic borylation reaction with BBr$_3$. The intermediate 2-(2-dibromoborylaryl) pyridines were stable enough to be handled in air and served as the synthetic platform for variously substituted quinoline–borane complexes. All the structures were fully characterized by spectral and analytical methods.[19] All of the N, C-chelate four-coordinate organoborons produced are stable in air and water, and can be purified by column chromatography on silica gel. These compounds have a high thermal stability; for example, the decomposition temperatures for a 5% weight loss (T$_{d5}$) of **4a** and **5a** are 335 °C and 298 °C, respectively.19



Condition I: 2-amino benzaldehydes (0.3 mmol), alkynes (0.36 mmol), PPh$_3$AuCl (5 mol %), AgOTf (5 mol %), *p*-anisidine (25 mol %), DCE (2 ml), 100 °C, 12 hrs, 80-95% ^{a}**Condition II**: Quinolines **2, 3, 4** and **6** (0.76 mmol), BBr$_3$ (2.29 mmol), DIPEA (0.76 mmol), CH$_2$Cl$_2$, rt, 24 hrs; ^{b}**Condition III**: i) Quinolines **1-6** (0.76 mmol), BBr$_3$ (2.29 mmol), DIPEA (0.76 mmol), CH$_2$Cl$_2$, rt, 24 hrs; ii) AlR$_3$ (1.68 mmol), toluene:CH$_2$Cl$_2$ (1:1), rt, 30 min. **Note**: Average yields starting from 2-substituted quinolines.

Scheme 1. Synthesis of N,C-chelate four-coordinate organoborons

The organoborons **1a** – **6e** showed intense fluorescence in solution and in the solid state. The photophysical data of complexes **1a** – **6e** recorded in CH$_2$Cl$_2$ and solid state (Table 1). All of the complexes exhibited a broad absorption band between 387 - 491 nm attributable to the electronic transition originating from the π-molecular orbitals. All the fluorophores exhibited intense emission in CH$_2$Cl$_2$ solutions when excited at their absorption maxima. The emission profiles of these complexes in solution, having emission bands that peaked at 466 nm (**1a**, blue) to 637 nm (**2c**, red), covered a wide range from blue to red, reflecting that the substituent at the two position of quinolines was indeed effective in tuning the emission color of this type of N,C-chelate four-coordinate organoborons (Fig 2c). The absolute fluorescence quantum yields in solutions were measured using an integrating sphere method. The N,C- chelate four-coordinate organoboron wherein the methyl groups exist on boron center showed good quantum yield (Φ$_f$ 0.81 for **3a**) as compared to those with bromo substituents (Φ$_f$ 0.03 for **2c**).

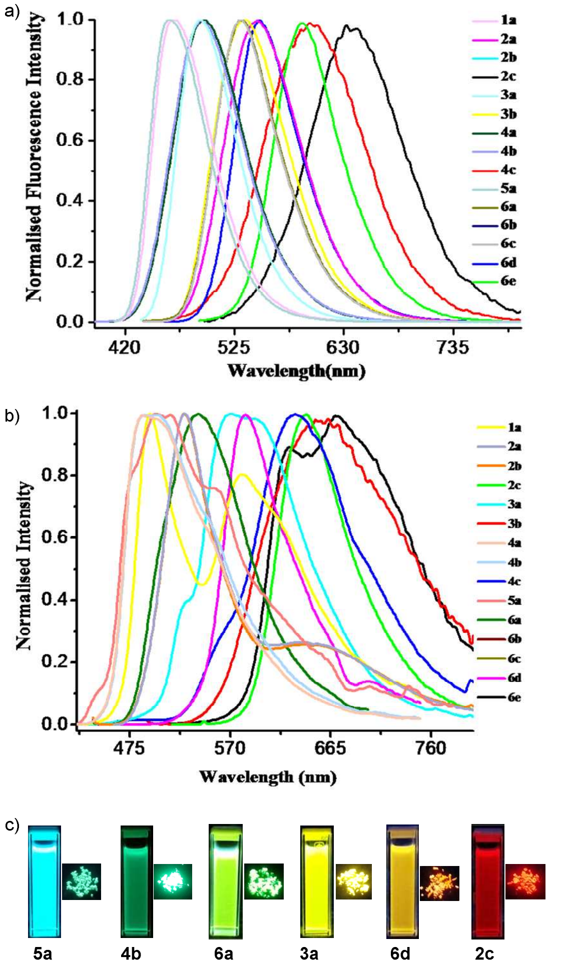


Figure 2. (a) Emission spectra (excited with longest absorption maxima) in CH$_2$Cl$_2$ and (b) Emission spectra in the solid state (powder) and (c) photographic images (excited at 365 nm using a UV lamp) of solution and solid compounds.

All complexes showed strong broad solid-state absorption in the UV-visible region between 397 - 496 nm and intense solid-state fluorescence emission between 491 - 670 nm (Fig 2b). The fluorescence of the solid samples with emission peaks at 491 nm (greenish blue for **1a**) and 670 nm (deep red for **6e**) also covered a wide range from blue to deep red (Fig 2c). The emission maxima of complexes **1a** – **6e** in solid state shows blue and red shifted compared with those of solution state which reflected crystallochromy effects. The wavelength of the emission maximum (λ$_{em}$) of **6d** (R = phenyl) and **6e** (R = Br) is red shifted by 44 nm and 130 nm than that of **6a** (R = Me) respectively and for **6a** (R = Me), **6b** (R = Ethyl) and **6c** (R = *n*-octyl) is almost similar which indicates the effect of substituent present at boron center with respect to quinoline π-framework. To evaluate the substitution effect on the photo-physical properties, the absorption and emission spectra of diphenylamine- and carbazole- substituted boron complexes **2a** and **4a** in CH$_2$Cl$_2$ and solid state were compared. These two complexes showed completely different absorption and emission properties merely due to the subtle difference in substitution, despite their structural similarity. As depicted in Fig. 2, the carbazole-substituted boron complex **4a** is greenish-blue emissive with an absorption band centred at 387 nm and an emission band which peaked at 497

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nm. Diphenylamine-substituted boron complex **2a** is greenish yellow fluorescent with the longest absorption maximum of 433 nm and emission band centred at 546 nm, exhibiting 46 and 49 nm red shifts for absorption and emission maxima compared to **4a**. Similarly in solid state **4a** shows emission at 491 nm and **2a** shows at 525 nm. According to density functional theory (DFT) calculations, the electron-donating group substituted at the para position significantly pushed the HOMO level up, hence narrowing the energy gap of the boron complex.[19] In view of these comparisons, it is clear that only the slight difference in the chemical structure, results in a significant difference in the photo physical properties of complexes. All the solid samples are highly emissive and their quantum yields were determined using an integrating sphere. The compound **4a** shows highest quantum yield (Φ_f 0.41) in solid state powder form with respect to other complexes. It should be noted that the N,C-chelate four-coordinate organoborons also showed positive solvatochromic behaviour as emission wavelengths were found to be red shifted with increase in solvent polarity.[19]

Table 1. Photophysical data

Comp	λ_{abs} (nm)^a CH$_2$Cl$_2$	solid^b	λ_{em}(nm)^c CH$_2$Cl$_2$	solid	Δ_{Stokes} (cm^{-1})^d CH$_2$Cl$_2$	solid	ϕ_f ^{e} CH$_2$Cl$_2$	solid	τ_f (ns)^f
1a	406	405	466	491	3170	4323	0.58	0.12	5.2
2a	433	466	546	525	4774	2412	0.56	0.18	6.4
2b	434	459	548	524	4791	2696	0.60	0.13	6.0
2c	491	502	637	642	4661	4343	0.03	0.14	2.1
3a	418	415	491	584	3553	6966	0.81	0.19	4.0
3b	463	470	543	654	3180	5980	0.60	0.11	4.8
4a	387	397	497	491	5709	4820	0.71	0.41	6.2
4b	387	401	492	497	5504	4809	0.67	0.38	6.1
4c	435	434	600	631	6313	7192	0.09	0.04	3.2
5a	405	429	463	507	3091	3590	0.78	0.13	5.5
6a	433	435	531	540	4257	4461	0.50	0.36	6.6
6b	432	439	531	542	4257	4319	0.59	0.32	6.2
6c	431	459	532	534	4403	3053	0.53	0.21	6.9
6d	452	473	549	584	3905	4016	0.43	0.05	6.9
6e	487	496	589	670	3552	5234	0.14	0.15	2.5

^{a}The maximum absorption bands more than 300 nm. ^{b}Spincoated film prepared from a CH$_2$Cl$_2$ solution. ^{c}Excited at the longest maximum absorption band in CH$_2$Cl$_2$ and powder form. ^{d}Stokes shift = The difference between higher energy absorption maximum and the emission maximum. ^{e}Absolute quantum yields were measured using an integrating sphere

The single crystal X-ray structure provides better understanding about the PL properties of the luminogens. The molecular packing patterns in the crystals of **2a** (CCDC 1408898), **3a** (CCDC 1408899), **4a** (CCDC 1408900) is displayed in Figure 3 and that of **5a** (CCDC 1408901) and **6b** (CCDC 1408902) are provided in the Supporting Information. Molecules of these compounds are closely packed in their respective crystals *via* face-to-face $\pi\cdots\pi$ stacking interactions with inter centroid distances ranging from 3.636(5) Å to 3.974(5) Å involving either quinoline-quinoline rings or phenyl-quinoline rings. All these hydrophobic forces work collectively to restrict the intramolecular rotation process and hence promote the radiative relaxation of the excited state, causing the molecules to exhibit fluorescence strongly. The luminescence properties were also rationalized by the DFT level of theory using B3LYP functional and 6-311G** basis set. The HOMO-LUMO gaps estimated from theoretical calculations were found to be in a good agreement with the experimental UV-vis values (Table 2).[19] In the case of organoborons **3a**, **4a**, **5a** the theoretical values are over estimated by 17.5%, 21.1% and 3.52% respectively, in compared to the experimental UV-Vis values. In addition, the dipole moment values are found to be correlate well with the planarity of the molecules.

Table 2. Comparison of UV absorption with the HOMO-LUMO gap calculated based on optimized crystal geometries

Method	UV	B3LYP/6-311G**				% Δ^a	Dipole moment	Geometry
Compound	Absorption (nm)	LUMO (Hartee)	HOMO (Hartee)	Gap (Hartree)	Gap (nm)		(Debey)	
3a	344	-0.09348	-0.2028	0.1093	417	17.5	4.03	Planar
4a	332	-0.09275	-0.2010	0.1082	421	21.1	5.98	Non-planar
5a	358	-0.08823	-0.2107	0.1225	372	3.52	3.52	Planar

^{a} % Δ = 100*(Gap - Absorption)/Gap

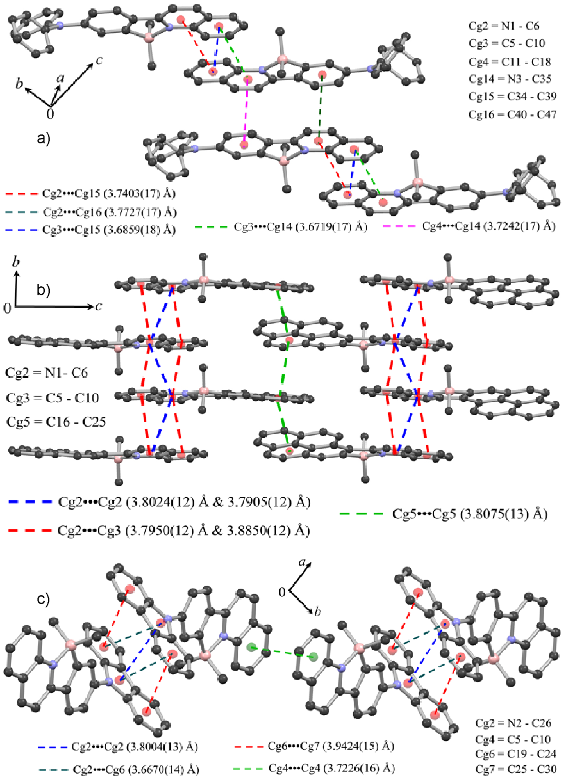

Figure 3. Single crystal packing of **2a** (a), **3a** (b) and **4a** (c)

Further, the feasibility of luminogens for biological imaging was studied by performing confocal imaging in MCF-7 cancer cell line which suggests that these N,C-chelate four-coordinate organoborons can successfully be exploited for *in vitro* bio-imaging.[19]

In summary, a series of highly emissive molecular solids based on N,C-chelate four-coordinate organoborons have been designed and synthesized. The results show the versatility of the 2-arylquinoline chelates for attaining an intense emission, with the maxima ranging over the whole visible region. The fluorophores have successfully marked MCF cells exhibiting their future potential as useful bioimaging fluorescence probes. Excellent photophysical properties combined with their thermal stability and DFT studies indicates that

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this class of compounds could have potential application in optoelectronic devices as well.

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