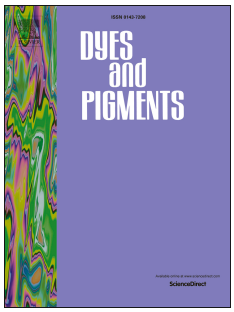


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Paramjit Kaur: Conceptulisation, Methdology, Writing original Draft

Kamaljit Singh: Validation of data, Supervision, Editing original Draft

Ishpreet Kaur: Experimental and data collection

Shivani: Experimental and data collection

# 2-(2'-Hydroxyphenyl)benzothiazole Derivatives: Emission and Colour tuning

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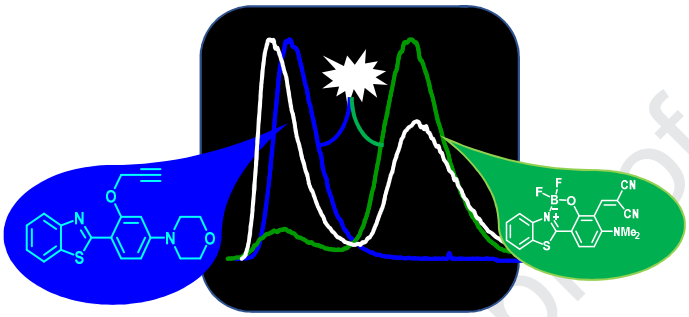

# 2-(2′-Hydroxyphenyl)benzothiazole Derivatives: Emission and Color tuning

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**Abstract:** Benzothiazole based molecular species are among the important heterocyclic compounds which are usually characterized by fluorescence that covers a wide spectral range. Herein, we present synthesis and luminescent behaviour of benzothiazole based derivatives and their rigidified boron(III) N^O chelates. Significant tuning of emission and absorption behaviour of the compounds led us to identify compositions of the complimentary colors emitted from these molecular species both in solution (CIE coordinates: x = 0.35753, y = 0.3315) as well as in the solid (CIE coordinates: x = 0.34753, y = 0.32062) state that furnished nearly white light emission. This work involving structurally simpler and easy to synthesise molecular species with different emission properties, importantly in the solid state, may find potential application in the context of colored and white-emitting materials.

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**Key words:** Benzothiazole; Boron(III) rigidified chelates; Multicolour emission; CIE coordinates; Broad range light emission.

## 1. Introduction

Synthesis of π-conjugated materials and tuning of their photophysical properties by structure modification as well as manipulation by way of supramolecular assembly and/or donor-acceptor dyads has led to identification of several functional π-systems [1]. Tuning of the

photophysical properties of such materials is manifested in absorption and emission behaviour, leading to their potential application in information displays, fluorescent sensors, optical recording systems [2]. Especially, the luminescent molecular assemblies, which can be tuned for white-light emission are of major importance because of their potential applications in lighting devices and display media [3-5]. The most common strategy adopted to tune the emissions is by combining primary or the dyes emitting complimentary colors [3, 6]. Among these, compounds exhibiting excited state intramolecular proton transfer (ESIPT) are widely used as these are often characterised by emission and absorption profiles covering a broad spectral range. Based upon the ESIPT concept, Park et al. [7] reported the first example of color tuning leading also to white light emission by combining blue and orange light emitters. Derivatives of 2-(2'-hydroxyphenyl)benzthiazole (HBT) are well known ESIPT compounds. In one of our recent publications [8], we have reported color-tunable HBT based chromophores exhibiting wavelength based reversible multicolour emission upon aggregation in solution as well as in the solid state. In continuation of our interest in boron containing systems such as 4,4-difluoro-4-bora-3*a*,4*a*-diaza-*s*-indacene (BODIPY) dyes [9], we envisaged, that the rigid systems obtained by locking N,N and N,O donor ligands as boron chelated complexes, may depict tuneable emission and colors especially in the solid state in line with the $BF_2$-hydrazine adducts reported in literature [10]. Borate chelation leading to emission changes has previously been reported in case of phenanthro[9,10-*d*]imidazole-quinoline-$BF_2$, naphthyridine-$BF_2$, pyridomethene-$BF_2$ and 2-(6'-hydroxy-5'-benzofuryl)$BF_2$ complexes [11-14].

In this paper, we report the design, synthesis and tuning of the emission colour of HBT based chromophores. Additionally, we have demonstrated that using binary combinations of HBT based chromophores, white light emission both in solution as well as in the solid state can be obtained. Using the additivity of mixing of colours, the current work

demonstrates the identification of formulations with emission spanning from blue to red region, including white emission.

## 2. Experimental

### 2.1. Materials and reagents

All liquid reagents were dried/purified using recommended drying agents and/or distilled over 4 Å molecular sieves. DMF, triethylamine and piperidine were dried, distilled and stored overnight over molecular sieves. Other solvents (analytical grade) used for the analytical work were purchased from Thomas Baker, while the ones used for the synthetic work were of synthesis grade. 4-Aminosalicylic acid, 1-bromo-2-(2-bromoethoxy)ethane, propargyl bromide and malononitrile were purchased from Sigma-Aldrich. Whereas $NaBH_3CN$, paraformaldehyde, NaH and $BF_3.OEt_2$ were purchased from Spectrochem and used as such. Solid state mixtures (**M1**-**M4**) were prepared by mixing **3** (0.001 g) with either **5** (0.001 g for **M1**; 0.0005 g for **M2**) or **6** (0.087 g for **M3**; 0.00113 g for **M4**) uniformly, with silica gel (0.001 g, 60-120 mesh) together with THF (10-20 mL) as annealing solvent.

### 2.2. Instrumentation

IR spectra were recorded on Cary 630 FTIR spectrophotometer of Agilent Technologies in the range 650–4000 $cm^{-1}$. Fluorescence studies were carried out using Perkin Elmer LS 55 and Fluorolog Horiba Fluorescence Spectrometer, having a pulsed xenon flash lamp (50–60 Hz) and a 450 W CW Ozone-free Xenon arc lamp (250 to 2500 nm) respectively. The fluorescence spectrometer consisted of Monk-Gillieson and Czerny-Turner type monochromators having 200–800 nm excitation range and 200–900 nm emission range and zero order R928 photomultiplier. The fluorescence spectroscopic studies were carried out using ultraviolet (UV) LED with excitation wavelengths of 340 nm, 400 nm and 440 nm (depending on compounds), focused perpendicularly to one side of the fluorescence quartz cuvette at excitation slit width of 12 nm. The emission spectrum was recorded by scanning

the monochromator in the visible region from 200 to 800 nm using emission slit width of 2.5 nm and 12 nm (depending on compounds), and detecting the optical signal using a photomultiplier tube located at the exit port of the monochromator, which was further connected to a power meter. Electronic absorption data was recorded on HITACHI U-2910 Spectrophotometers using matched quartz cuvettes with path length of 1 cm. The temperature of cell holder was maintained at 25±1˚C using a Peltier temperature controller. Mass spectrum (MS) was recorded on a Bruker HRMS MICROTOF II spectrometer. Melting points were determined in open capillaries and are uncorrected. $^{1}$H NMR and $^{13}$C NMR spectra were recorded on Bruker Avance II NMR spectrometer at 400 MHz and Bruker Biospin Avance III HD at 500 MHz, with TMS as internal standard using $CDCl_3$, DMSO-$d_6$ and $D_2O$ as solvents. Data are reported as follows: chemical shift in ppm (δ), integration, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant *J* (Hz) and assignment.

### 2.3. Computational details

All theoretical calculations were performed by using Gaussian09 suite of programmes [15]. The molecular geometries of the chromophores were optimised at the density functional theory (DFT) method employing the hybrid B3LYP functional group and the 6-31G(d) basis set. The first 30 excited states were calculated by using time-dependent density functional theory (TD-DFT calculations) in THF as solvent medium (CPCM) model. The molecular orbital contours were visualized using Gauss view 5.0.9.

### 2.4. Quantum yield calculations

The fluorescence quantum yields were calculated using 9,10-diphenylanthracene [16] as standard having quantum yield of 0.95 in cyclohexane, employing the following equation:

$$\Phi_u = \frac{F_u \times (1 - 10^{-A_s L_s}) \times n_u^2}{F_s \times (1 - 10^{-A_u L_u}) \times n_s^2} \times \Phi_s$$

where $\Phi_u$ and $\Phi_s$ are the quantum yields of the test and the standard samples, respectively. $A_u$ and $A_s$ are the absorbance values of the test sample and the standard sample, respectively, $F_u$ and $F_s$ are the areas of emission bands for the test sample and the standard sample, $n_u$ and $n_s$ are the refractive indices of test sample and standard sample solutions in their respective pure solvents. L is length of cell (1.0 cm for standard and test samples).

## 2.5. Synthetic procedures

### 2.5.1. Synthesis of 2-(4-amino-2-hydroxyphenyl)benzothiazole (1) [17]

An equimolar mixture of 4-aminosalicylic acid (18.3 mmol, 2.53 g) and 2-aminobenzenethiol (18.3 mmol, 2.00 g) in polyphosphoric acid (10 mL) was stirred at 180 $^{o}$C for 5 h. After cooling, the mixture was poured onto ice cold water and the precipitate was filtered, washed with water and dried using vacuum pump. The solid was purified by column chromatography using 10:90 (ethyl acetate/hexane; *v/v*) as eluant leading to 2.09 g of the product in 54% yield. M.p. = 210-213 $^{o}$C [17]. $^{1}$H NMR (300 MHz, DMSO-$d_6$) $\delta$/ppm: 5.0 (2H, s, -$NH_2$, $D_2O$ exchangeable), 5.2 (1H, s, ArH), 5.27 (1H, d, $J$ = 8.7 Hz, ArH), 6.37 (1H, t, $J$ = 7.8 Hz, ArH), 6.5 (1H, t, $J$ = 7.8 Hz, ArH), 6.66 (1H, d, $J$ = 8.7 Hz, ArH), 6.92 (1H, d, $J$ = 8 Hz, ArH), 7.05 (1H, d, $J$ = 7.8 Hz, ArH), 10.76 (1H, s, -OH, $D_2O$ exchangeable). $^{13}$C NMR (75 MHz, DMSO-$d_6$) $\delta$/ppm: 99.31, 106.3, 107.15, 120.82, 121.94, 124.32, 126.418, 130.03, 132.49, 151.857, 153.797, 158.79, 167.93.

### 2.5.2. Synthesis of 2-(4-morpholino-2-hydroxyphenyl)benzothiazole (2a)

To a solution of 2-(4-amino-2-hydroxyphenyl)benzothiazole **1** (0.2 g, 0.82 mmol) in DMF (10 mL) were added triethylamine (l mL) and 1-bromo-2-(2-bromoethoxy)ethane (0.52 mL, 4.12 mmol). The reaction mixture was heated at 140 $^{o}$C for 5-6 h and then the solution was diluted with ethyl acetate (100 mL). The solution was washed with saturated aqueous $Na_2CO_3$ solution (50 mL), the organic layer dried over anhydrous $Na_2SO_4$ and the solvent removed under reduced pressure. The residue was purified by column chromatography (1:9 ethyl

acetate/hexane) to afford **2a** as a yellow solid in 55% yield. M.p. = 175-180 $^{o}$C. IR (KBr): $\nu_{max}$ 3444.1, 3354.6, 3056.4, 2959.5, 2847.7, 2370.6, 2117.1, 1871.1, 1625.1, 1431.3, 1207.5, 976.6, 760.4, 596.4.$^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$/ppm: 7.90 (1H, d, $J$ = 10 Hz, ArH), 7.85 (1H, d, $J$ = 10.5 Hz, ArH), 7.54 (1H, td, $J_a$ = 11.5 Hz, $J_b$ = 2 Hz, ArH), 7.46 (1H, dt, $J_a$ = 10.0 Hz, $J_b$ = 1.5 Hz, ArH), 7.34 (1H, dt, $J_a$ = 10 Hz, $J_b$ = 1 Hz, ArH), 6.51 (1H, s, ArH), 6.48 (1H, d, $J$ = 3 Hz, ArH), 3.86 (4H, t, $J$ = 6 Hz, $CH_2$), 3.29 (4H, t, $J$ = 6 Hz, $CH_2$). $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$/ppm: 169.34, 159.63, 154.54, 152.14, 132.23, 129.65, 126.60, 124.89, 121.60, 121.49, 108.94, 106.82, 101.82, 77.36, 66.76, 47.85. HRMS: *m/z* calculated for $C_{17}H_{16}N_2O_2S$: 313.1005 $[M+1]^+$, Found: 313.0984 $[M+1]^+$.

**2.5.3. Synthesis of 2-(4-morpholino-2-(prop-2-yn-1-yloxy)phenyl)benzothiazole (3)**

To the suspension of NaH (0.05 g, 2.0 mmol) in DMF at 10 $^{o}$C, a solution of **2a** (0.5 g, 2.1 mmol) dissolved in DMF (10 mL) was added and stirred for 30 min at the same temperature. Propargyl bromide (0.5 g, 4.2 mmol) was added dropwise to the reaction mixture and stirred for 2 h for completion (TLC). The reaction mixture was then diluted with cold water and extracted with ethyl acetate. The organic layer was dried over anhydrous $Na_2SO_4$ and solvent was removed under reduced pressure to obtain crude **3**, which was further purified by column chromatography using 10:90 (ethyl acetate/hexane; *v/v*) as eluents to yield pure **3** in 63% yield. M.p. = 150-155 $^{o}$C. IR (KBr): $\nu_{max}$ 3265.1, 3056.4, 2967.0, 2847.7, 2318.4, 2117.1, 1595.3, 1431.3, 1237.5, 1185.3, 1118.2, 641.1. $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$/ppm: 8.40 (1H, d, $J$ = 11 Hz, ArH), 8.00 (1H, qd, $J_a$ = 10.5 Hz, $J_b$ = 1 Hz, ArH), 7.86 (1H, qd, $J_a$ = 10.0 Hz, $J_b$ = 1 Hz, ArH), 7.42 (1H, dt, $J_a$ = 10.0 Hz, $J_b$ = 1.5 Hz, ArH), 7.29 (1H, dt, $J_a$ = 9.5 Hz, $J_b$ = 1.5 Hz, ArH), 6.67 (1H, $J_a$ = 11.0 Hz, $J_b$ = 3 Hz, ArH), 6.64 (1H, d, $J$ = 3 Hz, ArH), 4.92 (2H, d, $J$ = 3 Hz, $CH_2$), 3.87 (4H, t, $J$ = 6 Hz, $CH_2$), 3.28 (4H, t, $J$ = 6 Hz, $CH_2$), 2.6 (1H, t, $J$ = 3 Hz, C≡C–H). $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$/ppm: 163.23, 156.61, 153.83, 152.27, 135.62, 130.59, 125.76, 124.06, 122.19, 121.12, 114.48, 108.66, 99.38, 78.05, 76.47, 66.64, 56.61,

48.10. HRMS: *m/z* calculated for $C_{20}H_{18}N_2O_2S$: 373.0981 $[M+Na]^+$, Found: 373.0867 $[M+Na]^+$.

**2.5.4. Synthesis of 2-(4-dimethylamino-2-hydroxyphenyl)benzothiazole (2b)**

To the stirred mixture of **1** (0.75 g, 2.60 mmol) and paraformaldehyde (0.39 g, 13.0 mmol) in glacial acetic acid (10 mL) at 0 °C, $NaBH_3CN$ (0.492 g, 7.80 mmol) was added in small portions. The mixture was allowed to warm up to room temperature and stirred overnight before being poured into cold water (150 mL). Formed solution was extracted with ethyl acetate (3x30 mL). Combined organic layer was washed with saturated aqueous $NaHCO_3$ solution and dried with anhydrous $Na_2SO_4$. Organic solvent was removed under reduced pressure and the obtained residue was purified by crystallization from ethanol to give the product **2b** in 80% yield. M.p. = 175-180 $^oC$; Anal. Found: C, 66.46; H, 5.32; N, 10.34; S, 11.74%, molecular formula $C_{15}H_{14}N_2OS$ requires: C, 66.64; H, 5.22; N, 10.36; S, 11.86%; IR (KBr): $\nu_{max}$ 3056.4, 2922.2, 2117.1, 1863.7, 1625.1, 1568.0, 1237.5, 969.1, 887.1, 745.5, 581.5, 454.7. $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$/ppm: 12.6 (1H, s, -OH, $D_2O$ exchangeable), 7.86 (1H, d, $J$ = 8 Hz, ArH), 7.81 (1H, d, $J$ = 8 Hz, ArH), 7.48 (1H, d, $J$ = 8 Hz, ArH), 7.42 (1H, t, $J$ = 7.5 Hz, ArH), 7.29 (1H, t, $J$ = 7.5 Hz, ArH), 6.31 (1H, d, $J$ = 8.5 Hz, ArH), 6.3 (1H, s, ArH), 3.05 (6H, s, N-$CH_3$). $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$/ppm: 169.75, 159.53, 153.74, 152.30, 132.08, 129.72, 126.41, 124.43, 121.37, 121.24, 106.53, 104.64, 98.79, 40.26.

**2.5.5. Synthesis of 2-(4-dimethylamino-3-formyl-2-hydroxyphenyl)benzothiazole (4)**

A mixture of DMF (3 mL, 0.0257 mol) and $POCl_3$ (3 mL, 0.0257 mol) was cooled in an ice bath and stirred under nitrogen atmosphere for 5 min. After warming to room temperature, the reaction mixture was further stirred for 30 min. Then, **2b** (1.4 g, 0.0052 mol) in 1,2-dichloroethane (140 mL) was added to the reaction mixture. After rising the temperature to 80 $^oC$, the reaction mixture was further stirred for 10 h, cooled to room temperature and slowly poured into a saturated aqueous solution of $K_2CO_3$ (200 mL) cooled in an ice bath.

After warming to room temperature, the reaction mixture was further stirred for 1 h and extracted with DCM. The organic layers were combined, washed with water, dried with anhydrous $NaSO_4$, and the solvent was removed under reduced pressure. The crude product was purified by silica gel (60-120 mesh) column chromatography using 30:70 (ethyl acetate/hexane; *v/v*) as the eluent to give the formylated product **4** as yellowish-brown powder. Yield 23%. M.p. = 105-110 $^{o}$C. IR (KBr): $\nu_{max}$ 3175.7, 2996.8, 2877.5, 2795.5, 2102.2, 1871.1, 1580.4, 1476.0, 1401.5, 1267.3, 1051.1, 760.4, 603.8, 544.2, 477.1. $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$/ppm: 13.52 (1H, s, -OH, $D_2O$ exchangeable), 10.28 (1H, s, -CHO), 8.16 (1H, s, ArH), 7.96 (1H, d, *J* = 8 Hz, ArH), 7.88 (1H, d, *J* = 8 Hz, ArH), 7.45 (1H, t, *J* = 7.5 Hz, ArH), 7.34 (1H, t, *J* = 7.5 Hz, ArH), 6.56 (1H, d, *J* = 8.5 Hz, ArH), 3.06 (6H, s, N-$CH_3$). $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$/ppm: 186.52, 151.83, 151.80, 126.22, 124.52, 121.81, 121.34, 111.28, 107.99, 44.98. HRMS: *m/z* calculated for $C_{16}H_{14}N_2O_2S$: 299.0849 $[M+H]^+$, Found: 299.0818 $[M+H]^+$.

**2.5.6. Synthesis of 2-(3-(benzothiazole-2-yl)-6-(dimethylamino)-2-hydroxybenzylidene) malononitrile (5)**

A solution of **4** (0.1 g, 0.33 mmol), piperidine (0.038 mL, 0.39 mmol) anhydrous THF (20 mL) under inert atmosphere was cooled to 0 $^{o}$C and a solution of malononitrile (0.048 g, 0.13 mmol) in anhydrous THF (1 mL) was added dropwise and the reaction stirred at 0 $^{o}$C until completion (TLC). After the completion of reaction, THF was removed under reduced pressure. And crude was washed with water (2x20 mL) and DCM, the organic layer was dried over anhydrous sodium sulphate. The solvent removed under reduced pressure to obtain crude **5**, which was purified by column chromatography using 35:65 (ethyl acetate/hexane; *v/v*) as eluents to isolate analytically pure **5** as yellowish orange solid. Yield 60%. M.p. = 200 $^{o}$C. IR (KBr): $\nu_{max}$ 3302.4, 3063.9, 2862.6, 2117.1, 1990.4, 1900.9, 1736.9, 1654.9, 1580.4, 1289.7, 1192.7, 939.3, 760.4, 626.2, 484.64. $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$/ppm: 8.54 (1H, d,

199 *J* = 8 Hz, ArH), 8.08 (1H, s, C=C–H), 8.068 (1H, d, *J* = 8.5 Hz, ArH), 7.96 (1H, s, -OH, $D_2O$
200 exchangeable), 7.95 (1H, d, *J* = 8 Hz, ArH), 7.52 (1H, t, *J* = 7.5 Hz, ArH), 7.42 (1H, t, *J* = 7.5
201 Hz, ArH), 6.88 (1H, t, *J* = 9 Hz, ArH), 3.01 (6H, s, N-$CH_3$). $^{13}$C NMR (125 MHz, DMSO-$d_6$)
202 $\delta$/ppm: 160.25, 155.04, 152.54, 152.07, 135.64, 134.47, 126.35, 125.11, 122.84, 121.42,
203 118.71, 114.87, 113.33, 77.23, 44.95. HRMS: *m/z* calculated for $C_{19}H_{14}N_4OS$: 347.0961
204 $[M+H]^+$, Found: 347.0774 $[M+H]^+$.

205 **2.5.7. Synthesis of (*E*)-2-(3-(3-(benzothiazole-2-yl)-6-(dimethylamino)-2-hydroxystyryl)-**
206 **5,5-dimethylcyclohex-2-en-1-ylidene)malononitrile (7)**

207 Similarly, using **4** (0.16 g, 0.33 mmol), piperidine (0.038 mL, 0.39 mmol) and 2-(3,5,5-
208 trimethyl-2-cyclohexenylidene)malononitrile (0.13 g, 0.7 mmol) in THF (10 mL) and stirring
209 the reaction at 40 $^o$C for 24 h furnished **7** as red solid, after extractive work up of the reaction
210 followed by purification as described above. Yield 30%. M.p. = 175-180 $^o$C. IR (KBr): $\nu_{max}$
211 3071.3, 3011.7, 2922.2, 2788.0, 2221.5, 2109.7, 1908.4, 1848.8, 1610.2, 1550.6, 1326.9,
212 1103.3, 998.9, 909.5, 797.7, 492.0. $^1$H NMR (500 MHz, $CDCl_3$) $\delta$/ppm: 13.83 (1H, s, -OH,
213 $D_2O$ exchangeable), 7.96 (1H, d, *J* = 8 Hz, ArH), 7.89 (1H, d, *J* = 8 Hz, ArH), 7.64 (1H, d, *J*
214 = 16.5 Hz, C=CH), 7.59 (1H, d, *J* = 8.5 Hz, ArH), 7.52 (1H, t, *J* = 8 Hz, ArH), 7.41 (1H, t, *J*
215 = 8 Hz, ArH), 7.35 (1H, d, *J* = 16.5 Hz, C=CH), 6.91 (1H, s, ArH), 6.66 (1H, d, *J* = 8.5 Hz,
216 ArH), 2.90 (6H, s, N-$CH_3$), 2.64 (2H, s, $CH_2$), 2.57 (2H, s, $CH_2$), 1.13 (6H, s, -$CH_3$). $^{13}$C
217 NMR (125 MHz, $CDCl_3$) $\delta$/ppm: 169.38, 158.75, 157.41, 156.33, 151.62, 132.44, 132.20,
218 132.03, 129.61, 126.86, 125.35, 122.92, 122.74, 121.77, 121.49, 115.39, 114.06, 111.13,
219 109.46, 44.45, 43.20, 38.95, 32.15, 28.22. HRMS: *m/z* calculated for $C_{28}H_{26}N_4OS$: 467.1900
220 $[M+H]^+$, Found: 467.1735 $[M+1]^+$.

221 **2.5.8. Synthesis of 2-((3-(dimethylamino)-6,6-difluoro-6*H*-6$\lambda^4$,7$\lambda^4$-**
222 **benzo[*e*]benzo[4,5]thiazolo[3,2-*c*][1,3,2]oxazaborinin-4-yl)methylene)malononitrile (6)**

To the solution of **5** (0.050 g) in DCM (4 mL) was added $Et_3N$ (52 µL) at room temperature. The resulting mixture was stirred for 30 min. After that $BF_3 \cdot OEt_2$ (54 µL) was added to the reaction mixture over a period of 15 min and the reaction was stirred until completion (TLC). The reaction mixture was then diluted with cold water and extracted with DCM. The organic layer was dried over anhydrous $Na_2SO_4$ and solvent was removed under reduced pressure to obtain crude **6**, which was further purified by column chromatography using 15:85 (ethyl acetate/hexane; *v/v*) as eluents to yield pure **6** as orange solid in 90% yield. M.p. = 220 $^oC$. IR (KBr): $\nu_{max}$ 3324.8, 2228.9, 1729.5, 1610.2, 1520.8, 1416.4, 1312.0, 1215.1, 1028.7, 767.8, 641.1, 521.8, 432.4. $^1H$ NMR (500 MHz, $CD_3CN$) $\delta$/ppm: 8.72 (1H, s, C=CH), 8.24 (1H, d, $J$ = 10 Hz, ArH), 8.20 (1H, d, $J$ = 8.5 Hz, ArH), 8.06 (1H, d, $J$ = 8.5 Hz, ArH), 7.79 (1H, t, $J$ = 8 Hz, ArH), 7.68 (1H, t, $J$ = 8 Hz, ArH), 7.06 (1H, d, $J$ = 9.5 Hz, ArH), 3.32 (6H, s, N-$CH_3$). $^{13}C$ NMR (125 MHz, DMSO-$d_6$) $\delta$/ppm: 160.18, 156.14, 155.17, 153.39, 151.61, 151.06, 134.96, 134.59, 126.53, 125.01, 122.31, 122.14, 115.15, 112.79, 110.78, 107.76, 96.02, 44.40. HRMS: *m/z* calculated for $C_{19}H_{13}BF_2N_4OS$: 433.0506 $[M+nK]^+$, Found: 433.0397 $[M+nK]^+$.

**2.5.9. Synthesis of (*E*)-2-(3-(2-(3-(dimethylamino)-6,6-difluoro-6*H*-6λ$^4$,7λ$^4$-benzo[*e*]benzo[4,5]thiazolo[3,2-*c*][1,3,2]oxazaborinin-4-yl)vinyl)-5,5-dimethylcyclohex-2-en-1-ylidene)malononitrile (8)**

Similarly, using **7** (0.050 g), $Et_3N$ (52 µL) and $BF_3 \cdot OEt_2$ (100 µL) in $CH_2Cl_2$ (4 mL) and stirring the reaction at room temperature for 3-4 h furnished **8** as red solid, after extractive work up of the reaction followed by purification as described above. Yield 90%. M.p. = 270-275 $^oC$. IR (KBr): $\nu_{max}$ 2922.2, 2214.0, 2117.1, 1871.1, 1736.9, 1483.5, 1326.9, 1110.7, 797.7, 626.2, 521.8. $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$/ppm: 8.28 (1H, d, $J$ = 10.5 Hz, ArH), 7.84 (1H, d, $J$ = 9.5 Hz, ArH), 7.62 (1H, dt, $J_a$ = 9.5 Hz, $J_b$ = 1.5 Hz, ArH), 7.51 (1H, dt, $J_a$ = 9.0 Hz, $J_b$ = 1.5 Hz, ArH), 7.48 (1H, d, $J$ = 11 Hz, ArH), 7.40 (1H, d, $J$ = 20.5 Hz, C=CH),

7.24 (1H, d, *J* = 20.5 Hz, C=CH), 6.84 (1H, s, ArH), 6.69 (1H, d, *J* = 11 Hz, ArH), 2.96 (6H, s, N-$CH_3$), 2.61 (2H, s, $CH_2$), 2.56 (2H, s, $CH_2$), 1.10 (6H, s, -$CH_3$). $^{13}$C NMR (125 MHz, $CDCl_3$) *δ*/ppm: 169.58, 159.79, 155.88, 154.81, 132.17, 131.08, 128.59, 127.90, 127.26, 126.67, 122.76, 121.84, 110.64, 106.50, 102.83, 92.71, 43.84, 43.18, 39.08, 32.04, 28.11. HRMS: *m/z* calculated for $C_{28}H_{25}BF_2N_4OS$: 515.1810 $[M]^+$, 537.1707 $[M+nNa]^+$, 553.1447 $[M+nK]^+$, Found: 515.1809 $[M]^+$, 537.1630 $[M+nNa]^+$, 553.1381 $[M+nK]^+$.

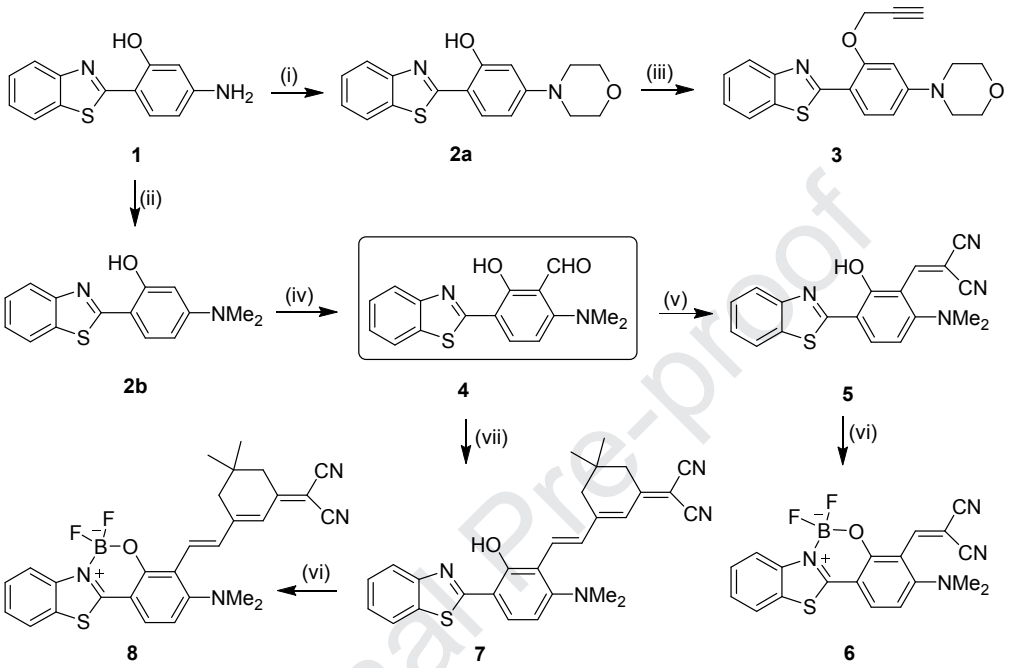
(Spectra shown in Figs. S1-S38, See ESI)

## 3. Results and Discussion

### 3.1. Synthesis

The synthesis of the target compounds started from reaction of 2-(4-amino-2-hydroxyphenyl)benzothiazole **1** with 1-bromo-2-(2-bromo ethoxy)ethane to obtain 2-(4-morpholino-2-hydroxyphenyl)benzothiazole **2a**. Compound **1** in turn was prepared from the reaction of 4-aminosalicylic acid and 2-aminobenzenthiol. Compound **2a** was efficaciously propargylated to 2-(4-morpholino-2-(prop-2-yn-1-yloxy)phenyl)benzothiazole **3** upon treatment with propargyl bromide under base catalysed reaction conditions (Scheme 1). Compound **1** was also reductively alkylated to obtain 2-(4-dimethylamino-2-hydroxy phenyl)benzothiazole **2b** in 80% yield. Vilsmeier-Haack formylation of **2b** yielded 2-(4-dimethylamino-3-formyl-2-hydroxyphenyl)benzothiazole **4**, which upon piperidine catalysed Knoevenagel condensation reaction with malononitrile and 2-(3,5,5-trimethylcyclohex-2-en-1-ylidene)malononitrile furnished compounds 2-(3-(benzothiazole-2-yl)-6-(dimethylamino)-2-hydroxybenzylidene)malononitrile **5** and (*E*)-2-(3-(3-(benzothiazole-2-yl)-6-(dimethylamino)-2-hydroxystyryl)-5,5-dimethylcyclohex-2-en-1-ylidene)malononitrile **7**, respectively. Finally, treatment of **5** and **7** with borontrifluoride etherate in anhydrous DMF in the presence of triethylamine gave 2-((3-(dimethylamino)-6,6-difluoro-6*H*-6$\lambda^4$, 7$\lambda^4$-benzo [*e*]benzo[4,5]thiazolo[3,2-*c*] [1,3,2]oxazaborinin-4-yl)methylene) malononitrile **6** and (*E*)-2-

(3-(2-(3-(dimethylamino)-6,6-difluoro-6*H*-6λ$^4$,7λ$^4$-benzo[*e*]benzo[4,5]thiazolo [3,2-*c*] [1,3,2] oxazaborinin-4-yl)vinyl)-5,5-dimethylcyclohex-2-en-1-ylidene)malononitrile **8**, respectively (Scheme 1). All compounds were characterized using spectroscopic ($^1$H NMR, $^{13}$C NMR, HRMS) data (Figs. S1-S38, See ESI).




**Scheme 1**. Reagents, reaction conditions and yield (%): (i) $Et_3N$/DMF (anhyd.)/1-bromo-2-(2-bromoethoxy)ethane/140 $^oC$ (55%); (ii) $NaCNBH_3$/paraformaldehyde/AcOH/r.t. (80%); (iii) NaH/DMF (anhyd.)/propargyl bromide /r.t. (63%); (iv) DMF/$POCl_3$/80 $^oC$ (23%); (v) THF (anhyd.)/piperidine/malononitrile/0 $^oC$/$N_2$ (60%); (vi) $BF_3.OEt_2$/DCM/$Et_3N$/r.t. (90%); (vii) 2-(3,5,5-trimethylcyclohex-2-en-1-ylidene)malononitrile/THF/piperidine, 40 $^oC$, $N_2$ (30%).

### 3.2. Optical properties

Compounds **1**-**8** showed structure dependent absorption as well as emission behaviour (Fig. 1) (For detailed spectra, see Fig. S39 in ESI). Thus, replacing $NH_2$ group in **1** with morpholino or $NMe_2$ in **2a** and **2b** saw low energy shift in the absorption band of **1** at 358 nm

(1 x $10^{-5}$ M in THF) to appear at 376 and 366 nm, respectively. Compound **5** shows two bands: at 338 nm ($\varepsilon_{max}$: 52400 molcm$^{-1}$L$^{-1}$) and 418 nm ($\varepsilon_{max}$: 9000 molcm$^{-1}$L$^{-1}$) attributed to π-π* (H→L+1 and H→L) transitions, respectively. The latter observed low energy shift to appear at 442 nm ($\varepsilon_{max}$: 6200 molcm$^{-1}$L$^{-1}$) in the oxazaborinin compound **6**.

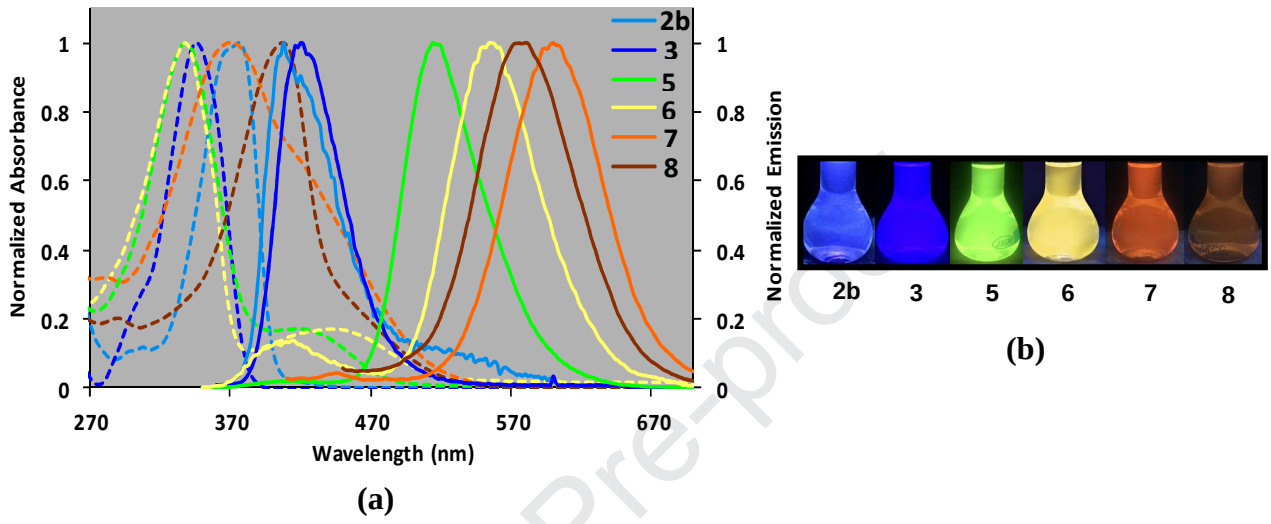



**Fig. 1** (a) UV-visible absorption spectra (dotted line) of **2b**, **3**, **5**-**8** (1 x $10^{-5}$ M in THF) and fluorescence emission spectra (solid line) of **2b**, **3**, **5**-**8** (1 x $10^{-5}$ M in THF); (b) Photographs of respective solutions under illumination at 365 nm.

Likewise, compound **7** showed major absorption band at 370 nm ($\varepsilon_{max}$: 62,100 molcm$^{-1}$L$^{-1}$) (H-2→L, π-π*), the corresponding oxazaborinin derivative **8** showed intense band at 408 nm ($\varepsilon_{max}$: 1,56,900 molcm$^{-1}$L$^{-1}$; H-1→L, π-π*) attesting to significant low energy shift as well as increase in extinction coefficient in the oxazaborinin. The bathochromic shifts observed in oxazaborinin **6** and **8** relative to corresponding non-chelated **5** and **7** respectively, are well supported by the TD-DFT calculations (Fig. 2) (Fig. S40, see ESI). The π-π* bands of these compounds did not show a regular trend in solvent dependence in the absorption spectra recorded in solvents of different polarity, nor was any solvatofluorism trend observed (Fig. S41-45, Tables S7, S8, See ESI).

These compounds showed contrasting yet interesting emission behaviour (Fig. 1). The compound **1** showed emission bands at 402 nm and 520 nm, corresponding to *enolic* and *keto* emission of the typical ESIPT chromophores.

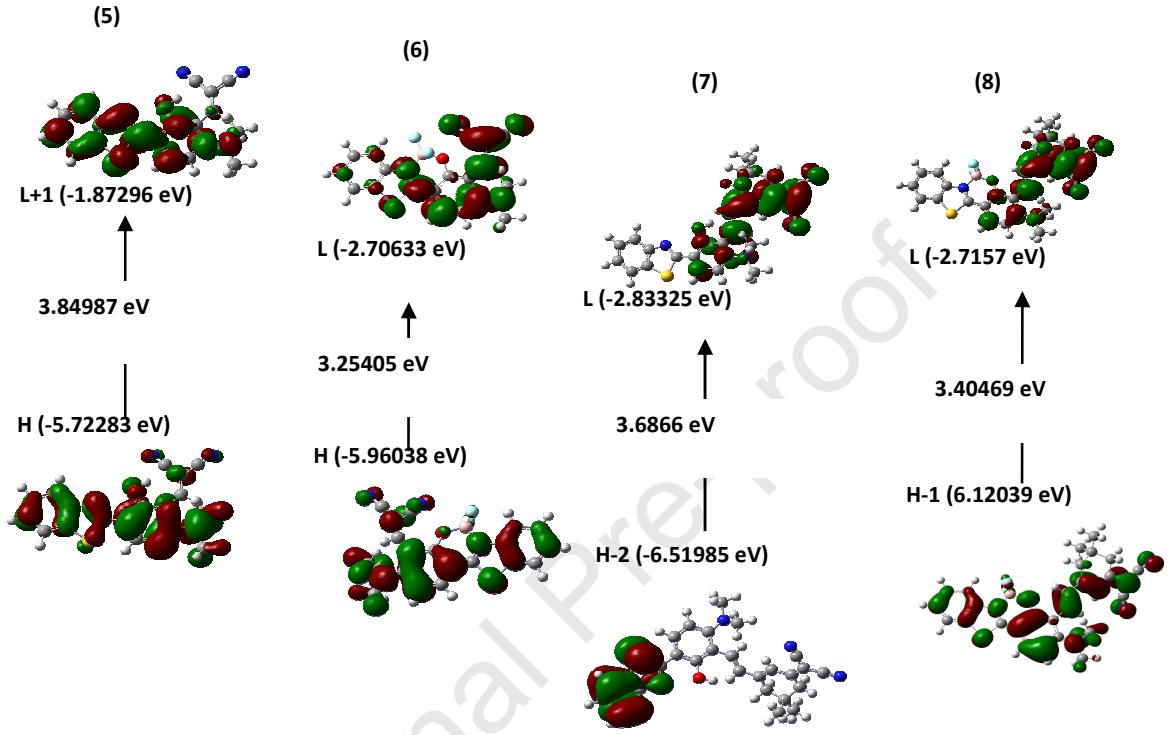



**Fig. 2** The contour surfaces of the frontier molecular orbitals HOMO (H) and LUMO (L) contributing to the electronic transitions of **5-8** obtained by TD-DFT calculations using B3LYP/6-31G (d)/CPCM/ THF phase at an isovalue of 0.02. (Fig. S40, See ESI)

Compounds where $NH_2$- group was replaced with a strong electron donor: morpholino (**2a**) or $Me_2N$ (**2b**) and when the OH was converted into *o*-propargyl group (**3**) showed only enolic emission at 408 nm (**2a**, **2b**) and 420 nm (**3**). Owing to structural features, chromophores appended with electron withdrawing groups: dicyanovinylidene in **5**, 5,5-dimethylcyclohex-2-en-1-ylidene malononitrile in **7** or the chelated counterparts: oxazaborinins **6** and **8** showed emission at unexpectedly lower energy (Fig. 1)

compared to CHO appended **4**, which showed both enolic as well as keto emission at 465 nm and 517 nm, respectively (For detailed spectra see Fig. S39 in ESI).

Compounds **5** and **7** show green and yellowish-orange emission at 514 nm and 600 nm when excited at 340 nm and 400 nm, respectively (Fig. 1). The blue shift of 6 nm in the emission band of **5** in comparison to the compound **1** is believed to be due to the deviation of the benzothiazole unit from coplanarity with the remainder of the molecule in compound **5** as predicted by the dihedral angles (Fig. S46). The oxazaborinin derivatives **6** and **8** show emission bands at 557 nm and 582 nm ($\lambda_{exc}$: 340 nm and 440 nm, respectively), corresponding to yellow and orange colours, respectively. The blue shift observed in the emission band of 8 in comparison to 7 is believed to be due to the perturbation in the π-conjugation on complexation with boron(III). The quantum yields in THF are given in the Table 1 (For the fluorescence quantum yields in various solvents see Table S9 in ESI).

In combination with a blue emitting compound such as **3** ($\lambda_{em}$: 420 nm; $\lambda_{exc}$: 300 nm), chromophores **5-7** were expected to yield a complementary combination covering emission in the range 420-600 nm, yielding nearly white overall emission. White light emission from a single molecular system has been very challenging and is scarcely reported [18-22], while the independent emission of red, blue and green fluorophores grafted in a covalent conjugate, is often hampered by the operation of either intramolecular Foster Resonance Energy Transfer (FRET) and/or Through Bond Energy Transfer (TBET) [23-26]. Thus, identification of white light emitting binary or ternary combination of materials is highly sought after and challenging task. Literature records several instances of white light emission wherein combination of materials emitting different colours have been combined as represented by supramolecular assemblies [4a], polymers [27,28], dye-doped soft materials such as organogels

[6b,29-31] or even composites [32,33]. Many such systems are based on photo-physical processes such as ESIPT [34], intramolecular charge transfer (ICT) [35,36] or operation of tautomerization [37-39] by pH control and aggregation leading to existence of molecules in more than one form, each displaying its discrete emission properties. This prompted us to calculate chromaticity coordinates of these compounds and to formulate a suitable combination, which upon mixing in a specific proportion would yield white emission. The chromaticity coordinates were calculated using the method recommended by CIE by summation (360-780 nm) of the emission data, relative energy distribution of the CIE standard $D_{65}$ illuminant and colour matching functions corresponding to CIE 1931 standard ($2^{o}$) observer. While the emission behaviour of the solutions of the chromophores and their representative combinations, relevant to white emission production are shown in Fig. 3a,b (Fig. S47, See ESI) their placement in the CIE chromaticity diagram, plotted using chromaticity coordinates (x and y) corresponding to $D_{65}$ is shown in Fig. 3c. Since the line joining the points corresponding to **3** (x = 0.1636; y = 0.0418) and **6** (x = 0.3887; y = 0.5368) in the chromaticity diagram passes through the white region corresponding to the illuminant $D_{65}$, these colours constitute complementary spectral colours and their combination, **M7** (3:6, 1.5:8.5 *v*/*v*) corresponded to white emission (x = 0.35753, y = 0.3315) (Table 1). Interestingly, emission of this combination covered full spectral region ranging from 400-700 nm with prominent dual emission at 398 nm and 564 nm (Fig. 3b). Further, since the absorption and emission behaviour of **3** and **6** operate independently (no energy transfer) the dual emission bands of the combination **M7** represent a superposition of the individual emission bands of **3** (420 nm) and **6** (557 nm) (Fig. S48, See ESI) pointing to the production of a stable white emission from **M7**. Similarly, wavelength of maximum absorbance of **M7** in THF was at 338 nm, which is

comparable to both **3** (346 nm) and **6** (338 nm). On the contrary, combination of **3**, **5** and **7** (**M1**), consisting of chromophores lacking oxazaborinin ring did not produce as white emission as **M7**, as it lacked significant red emission. Thus, oxazaborinin ring is seen to enhance red emission, leading to white light emission by the mixture **M7** (Fig. 3d) (For the Stokes shifts see the Table S 10 in ESI).

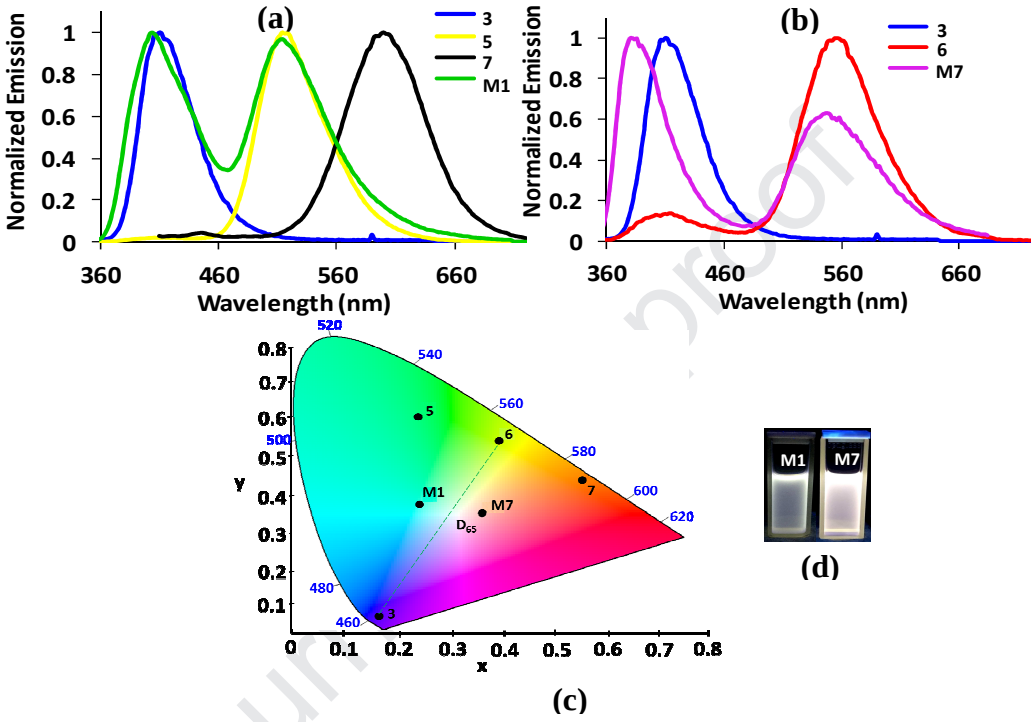



**Fig. 3** Fluorescence emission spectra of (a) **3**, **5** and **7** (1 x $10^{-5}$ M) and their mixture **M1** (**3**:**5**:**7**, 1:1:3, *v*/*v*; 5 x $10^{-5}$ M); (b) **3** and **6** (1 x $10^{-5}$ M) and their mixture **M7** (**3**:**6**, 1.5:8.5 *v*/*v*; 5 x $10^{-5}$ M) in THF; (c) placement of the colors in the CIE chromaticity diagram (1931, $D_{65}/2^{o}$ observer) based on the emission of respective solutions. The line connecting **3** and **6** passes through white region of standard illuminant; (d) Photographs of **M1** and **M7** in THF under illumination at 365 nm.

In order to probe the white light emission in the solid state, we recorded fluorescence emission spectra of solid admixture of the compounds (0.001 g) as well as their combinations, mixed uniformly, with silica gel (0.001 g, 60-120 mesh) using THF as annealing solvent. The emission profile of the compounds (Fig. 4, Fig. S49) reveals

emission covering blue (**3**: $\lambda_{em.}$ 445 nm, $\lambda_{exc.}$ 300 nm), yellow (**5**: $\lambda_{em.}$ 575 nm, $\lambda_{exc.}$ 340 nm), yellowish-orange (**6**: $\lambda_{em.}$ 601 nm, $\lambda_{exc.}$ 400 nm), orange-red (**7**: $\lambda_{em.}$ 695 nm, $\lambda_{exc.}$ 440 nm) and red (**8**: $\lambda_{em.}$ 711 nm, $\lambda_{exc.}$ 400 nm) regions.

**Table 1.** CIE chromaticity coordinates (x,y) and the quantum yields of **3**, **5-8** and various mixtures in THF.

| Code (in CIE diagram) | Compound/ mixture | Ratio (*v*/*v*) | CIE chromaticity coordinates (x,y) | Quantum yield ($\Phi_f$) |
|---|---|---|---|---|
| 3 | 3 | - | 0.16365, 0.0418 | 0.308[a] |
| 5 | 5 | - | 0.23773, 0.60629 | 0.394[b] |
| 6 | 6 | - | 0.38876, 0.53679 | 0.247[b] |
| 7 | 7 | - | 0.54435, 0.42603 | 0.335[b] |
| 8 | 8 | - | 0.47834, 0.49258 | 0.163[b] |
| M1 | 3+5+7 | (1 : 1 : 3) | 0.24032, 0.35897 | 0.048[a] |
| M2 | 3+5+7 | (2 : 1: 2) | 0.20122, 0.21411 | 0.097[a] |
| M3 | 3+5+7 | (1: 3 : 1) | 0.25126, 0.44117 | 0.134[a] |
| M4 | 3+5+7 | (3 : 1: 1) | 0.18227, 0.13384 | 0.135[a] |
| M5 | 3+6 | (1 : 1) | 0.23027,0.15187 | 0.019[a] |
| M6 | 3+6 | (1 : 4) | 0.26486,0.21156 | 0.002[a] |
| **M7** | **3+6** | **(1.5 : 8.5)** | **0.35732,0.3315** | 0.0055[a] |
| M8 | 3+6 | (1 : 9) | 0.3737,0.39259 | 0.0089[a] |

[a]9,10-Diphenylanthracene was used as a reference dye ($\Phi_f$ = 0.90 in cyclohexane). [b]Fluorescein was used as a reference dye ($\Phi_f$ = 0.79 in 0.1M aqueous NaOH).

The bathochromic shift in the emission of compounds **5-8** ($\lambda_{em}$: 575-711 nm) in solid state in comparison to **3** ($\lambda_{em}$: 445 nm) is attributed to the stabilisation of the excited state due to the presence of electron withdrawing groups in analogy with the observation in solution phase emission pattern. Further, the red tuning of the emission in **6** and **8** in comparison to their corresponding compounds **5** and **7** respectively, can be attributed to the additional contribution from the boron(III) atom in rigidifying the chromophore, thereby extending the

planarity and charge delocalisation along the major molecular axis. It is well supported by the molecular geometries and the small dihedral angles calculated by DFT calculations (Fig. S46, See ESI).

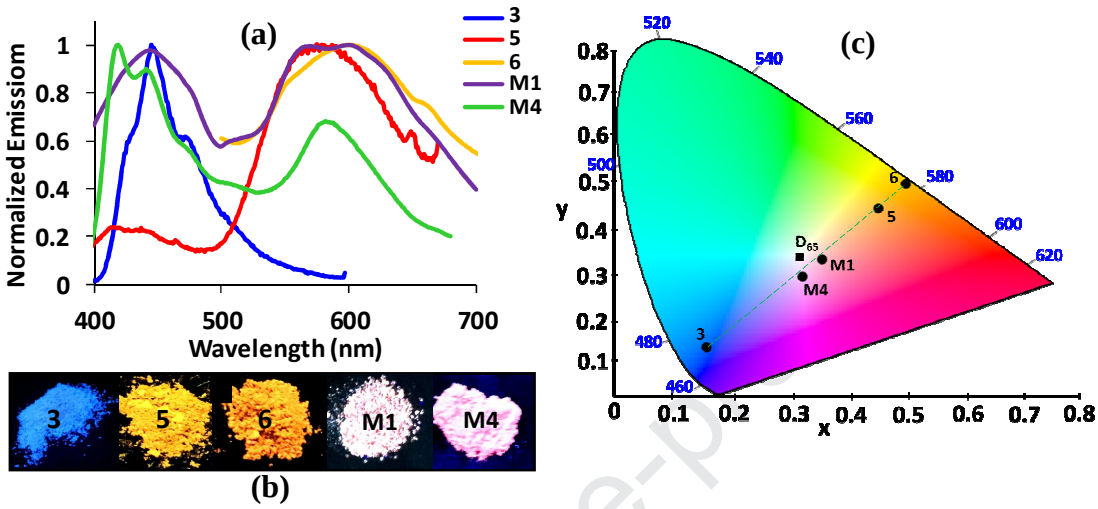



**Fig. 4** (a) Fluorescence emission of **3**, **5**, **6** and their mixtures **M1** (**3**:**5**, 1:1 *w*/*w*) and **M4** (**3**:**6**, 1:1.2 *w*/*w*) in solid state; (b) Photographs of respective compounds and mixtures under illumination at 365 nm and (c) placement of the colours in the CIE chromaticity diagram (1931, $D_{65}$/2 degree observer) based on the emission of respective solutions. The line connecting **3** with **5** and **6** passes through white region of standard illuminant.

Considering the complementarity of the blue color with orange, we formulated different combination of **3** with **5** and **6** in the solid state and placing these in the CIE chromaticity diagram revealed that the line connecting the point corresponding to **3** with **5** or **6**, passes through the white region corresponding to $D_{65}$. However, the best white emission was obtained from the 1:1 blend of **3** with **5**, represented by the blend **M1** for which the CIE chromaticity coordinates were x = 0.34753 and y = 0.32062 (Fig. 4c) (Table 2). Similarly, **M4** representing a combination of **3** and **6** (1:1) yielded white color corresponding to x = 0.31484 and y = 0.2806.

**Table 2.** CIE chromaticity coordinates (x,y) of **3**, **5-8** and various mixtures in solid state.

| Sr. no. | Code (in CIE diagram) | Compound/ mixture | Ratio (*w*/*w*) | CIE chromaticity coordinates (x,y) |
|---|---|---|---|---|
| 1 | 3 | 3 | - | 0.15393, 0.11655 |
| 2 | 5 | 5 | - | 0.44138, 0.43952 |
| 3 | 6 | 6 | - | 0.48693, 0.4966 |
| 4 | 7 | 7 | - | 0.67264, 0.31961 |
| 5 | 8 | 8 | - | 0.56116, 0.31666 |
| **6** | **M1** | **3+5** | **(1 : 1)** | **0.34753, 0.32062** |
| 7 | M2 | 3+5 | (2 : 1) | 0.26585, 0.25242 |
| 8 | M3 | 3+6 | (1.3 : 1) | 0.2404, 0.1695 |
| 9 | M4 | 3+6 | (1 : 1) | 0.31484, 0.2806 |

## 4. Conclusion

In summary, here we present a case of arresting ESPIT of benzothiazole based ESIPT chromophores by substitution of the phenyl ring with electron withdrawing groups and/or locking the ESIPT sites as oxazaborin in rings. This case is unique and different from earlier reports as in those reports either ESIPT was employed to circumvent the energy transfer between two chromophores [26] or through modulation of photoluminescence quantum yields by forming N^O chelates [40]. Our case presents an example of additive mixing of solutions as well as solid colours to produce white light emission.

## 5. Acknowledgements

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**Supporting Information**

Spectral data, photophysical studies/data, optimized structures, DFT/TD-DFT calculations, and complete reference of Gaussian09 [15].

**References**

[1] (a) L. C. Palmer, S. I. Stupp, Molecular self-assembly into one-dimensional nanostructures, Acc. Chem. Res. 41 (2008) 1674-84; (b) V. L. Malinovskii, D. Wenger, R. Haner, Nucleic acid–guided assembly of aromatic chromophores, Chem. Soc. Rev. 39 (2010) 410-22; (c) K. Singh, D. Sareen, P. Kaur, H. Miyake, H. Tsukube, Materials based receptors: Design, Principle and Applications, Chem. Eur. J. 19 (2013) 6914-36; (d) S. Kaur, M. Kaur, P. Kaur, K. Clays, K. Singh, Ferrocene chromophores continue to inspire. Fine-tuning and switching of the second-order nonlinear optical response, Coord. Chem. Rev. 343 (2017) 185-219.

[2] (a) X. L. Ni, S. Chen, Y. Yanga, S. Reineke, F. Lindner, G. Schwartz et al., White organic light-emitting diodes with fluorescent tube efficiency, Nature 459 (2009) 234-39; (b) G. M. Farinola, R. Ragni, Electroluminescent materials for white organic light emitting diodes, Chem. Soc. Rev. 40 (2011) 3467-82.

[3] Y. Yang, T. Wang, P. Yin, W. Yin, S. Zhang, Z. Lei et al., A general concept for white light emission formation from two complimentary colored luminescent dyes, Mater. Chem. Front. 3 (2019) 505-12.

[4] (a) D. Li, J. Wang, X. Ma, White light emitting materials constructed from supramolecular approaches, Adv. Optical Mater. 6 **(**2018) 1800273; (b) S. Wang, L. Zhao, B. Zhang, J. Ding, Z. Xie, L. Wang et al., High-energy-level blue phosphor for solution-processed white organic light-emitting diodes with efficiency comparable to fluorescent tubes, iScience 6 (2018) 128-37; (c) S. Shao, S. Wang, X. Xu, Y. Yang, J. Lv, J. Ding et al. Chem. Sci. 9 (2018) 8656-64.

[5] S. Mukherjee, P. Thilagar, Organic white light emitting materials, Dyes Pigm. 110 **(**2014) 2-27.

[6] (a) D. K. Maiti, R. Bhattacharjee, A. Datta, A. Banerjee, Modulation of fluorescence resonance energy transfer efficiency for white light emission from a series of stilbene-perylene based donor-acceptor pair, J. Phys. Chem. C 117 (2013) 23178-89; (b) C. Vijayakumar, V. K. Praveen, A. Ajayaghosh, RGB emission through controlled donor self-assembly and modulation of excitation energy transfer: A novel approach to white light emitting organogels, Adv. Mater. 21 (2009) 2059-63.

[7] S. Park, J. E. Kwon, S. H. Kim, J. Seo, K. Chung, S.-Y. Park et al., A White-light-emitting molecule: frustrated energy transfer between constituent emitting centers, J. Am. Chem. Soc. 131 (2009) 14043-49.

[8] I. Kaur, V. Sharma, S. M. Mobin, P. Kaur, K. Singh, Excitation wavelength based reversible multicolour photoluminescence by a single chromophore upon aggregation: detection of picric acid-application in bioimaging, Sens. Actuators B: Chemical, 281 (2019) 613-22.

[9] (a) P. Kaur, K. Singh, Recent advances in application of BODIPY in bioimaging and chemosensing, J. Mater. Chem. C 7 (2019) 11361-11405; (b) N. Kaur, P.

Kaur, K. Singh, Ferrocene-BODIPY push-pull dyad: A common platform for the sensing of $Hg^{2+}$ and $Cr^{3+}$, Sens. Actuators B: Chemical 229 (2016) 499-505; (c) N. Kaur, P. Kaur, G. Bhatia, K. Singh, J. Singh, Indole-BODIPY: a "turn-on" chemosensor for $Hg^{2+}$ with application in live cell imaging, RSC Advances 6 (2016) 82810-16.

[10] Y. Yang, X. Su, C. N. Carroll, I. Aprahamian, Aggregation-induced emission in $BF_2$–hydrazone (BODIHY) complexes, Chem. Sci. 3 (2012) 610-13.

[11] Y. Kubota, T. Tsuzuki, K. Funabiki, M. Ebihara, M. Matsui, Synthesis and fluorescence properties of a pyridomethene−$BF_2$ Complex, Org. Lett. 12 (2010) 4010-13.

[12] W. Li, W. Lin, J. Wang, X. Guan, Phenanthro[9,10-*d*]imidazole-quinoline boron difluoride dyes with solid-state red fluorescence, Org. Lett. 15 (2013) 1768-71.

[13] L. Quan, Y. Chen, X.-J. Lv, W.-F. Fu, Aggregation□induced photoluminescent changes of naphthyridine–$BF_2$ complexes, Chem. Eur. J. 18 (2012) 14599-604.

[14] J. Massue, D. Frath, P. Retailleau, G. Ulrich, R. Ziessel, Synthesis of Luminescent 2-(2′-Hydroxyphenyl)benzoxazole (HBO) Borate Complexes, Org. Lett. 14 (2012) 230-33.

[15] M. J. Frisch et al. Gaussian 09, Revision B.01, Gaussian, Inc., Wallingford CT, 2010 (For complete ref. see ESI)

[16] A. M. Brouwer, Standards for photoluminescence quantum yield measurements in solution (IUPAC Technical Report), Pure Appl. Chem. 83 (2011) 2213-28.

[17] F.S. Santos, E. Ramasamy, V. Ramamurthy, F.S. Rodembusch, Confinement effect on the photophysics of ESIPT fluorophores, J. Mater. Chem. C 4 (2016) 2820-27.

[18] D. Tu, P. Leong, S. Guo, H. Yan, C. Lu, Q. Zhao, Highly emissive organic single-molecule white emitters by engineering *o*-carborane-based luminophores, Angew. Chem. Int. Ed. 56 **(**2017) 11370-74.

[19] Q.-Y. Yang, J.-M. Lehn, Bright white-light emission from a single organic compound in solid state, Angew. Chem. Int. Ed. 53 (2014) 4572-77.

[20] Z. Xie, C. Chen, S. Xu, J. Li, Y. Zhang, S. Liu et al., White light emission strategyof a single organic compound with aggregation induced emission and delayed fluorescence property, Angew. Chem. Int. Ed. 54 (2015) 7181-84.

[21] S. Samanta, U. Manna, G. Das, White light emission from simple AIE-ESIPT-Excimer tripled molecular system, New J. Chem. 41 (2017) 1064-72.

[22] D. Li, W. Hu, J. Wang, Q. Zhang, X.-M. Cao, X. Ma, H. Tian, White light emission from a single organic compound with unique self-folded conformation and multistimuli responsiveness, Chem. Sci. 9 (2018) 5709-15.

[23] G.-S. Jiao, L. H. Thoresen, K. Burgess, Fluorescence through-bond energy transfer cassettes for labelling multiple biological molecules in one experiment, J. Am. Chem. Soc. 125 (2003) 14668-69.

[24] X. Zhang, M. A. Ballem, Z.-J. Hu, P. Bergman, K. Uvdal, Nanoscale light harvesting metal-organic frameworks, Angew. Chem. Int. Ed. 50 (2011) 5729-33.

[25] A. Ajayaghosh, V. K. Praveen, C. Vijayakumar, Organogels as scaffolds for excitation energy transfer and light harvesting, Chem. Soc. Rev. 37 (2008) 109-22.

[26] V. K. Praveen, C. Ranjith, E. Bandini, A. Ajayaghosh, N. Armaroli, Oligo(phenylenevinylene)hybrids and self-assemblies: versatile materials for excitation energy transfer, Chem. Soc. Rev. 43 (2014) 4222-42.

[27] S. Shinde, S. K. Asha, Temperature sensitive emission color tuning and white light emission in segmented OPV polymer: Perylene biimide supramolecular complex, Macromolecules 49 (2016) 8134-45.

[28] P. T. Furuta, L. Deng, S. Garon, M. E. Thompson, J. M. J. Frechet, Platinum-Functionalized Random Copolymers for Use in Solution-Processible, Efficient, Near-White Organic Light-Emitting Diodes. J. Am. Chem. Soc. 126 (2004) 15388-89.

[29] P. Bairi, B. Roy, P. Chakraborty, A. K. Nandi, Co-assembled white-light-emitting hydrogel of melamine, ACS Appl. Mater. Interfaces 5 (2013) 5478-85.

[30] S. S. Babu, V. K. Praveen, A. Ajayaghosh, Functional π-gelators and their applications, Chem. Rev. 114 (2014) 1973-2129.

[31] V. K. Praveen, C. Ranjith, N. Armaroli, White-light-emitting supramolecular gels, Angew. Chem. Int. Ed. 53 (2014) 365-68.

[32] Y.-L. Lei, Y. Jin, D.-Y. Zhou, W. Gu, X.-B. Shi, L.-S. Liao et al., White-light emitting microtubes of mixed organic charge-transfer complexes. Adv. Mater. 24 (2012) 5345-51.

[33] X. Wang, Y. Xu, X. Ma, H. Tian, Multicolor photoluminescence of a hybrid film via the dual-emitting strategy of an inorganic fluorescent Au nanocluster and an organic room-temperature phosphorescent copolymer, Ind. Eng. Chem. Res. 57 (2018) 2866-72.

[34] V. S. Padalkar, S. Seki, Excited-state intramolecular proton-transfer (ESIPT)-inspired solid-state emitters, Chem. Soc. Rev. 45 (2016) 169-202.

[35] W. Rettig, Charge separation in excited states of decoupled systems-TICT compounds and implications regarding the development of new laser dyes and the

primary process of vision and photosynthesis, Angew. Chem. Int. Ed. 25 (1986) 971-88.

[36] Z. R. Grabowski, K. Rotkiewicz, W. Rettig, Structural changes accompanying intramolecular electron transfer: focus on twisted intramolecular charge-transfer states and structures, Chem. Rev. 103 (2003) 3899-4032.

[37] Y. Yang, M. Lowry, C. M. Schowalter, S. O. Fakayode, J. O. Escobedo, X. Xu et al., An Organic White Light-Emitting Fluorophore, J. Am. Chem. Soc. 128 (2006) 14081-92.

[38] H. V. Huynh, X. He, T. Baumgartner, Halochromic generation of white light emission using a single dithienophosphole luminophore, Chem. Commun. 49 (2013) 4899-4901.

[39] D. Liu, Z. Zhang, H. Zhang, Y. Wang, A novel approach towards white photoluminescence and electroluminescence by controlled protonation of a blue fluorophore, Chem. Commun. 49 (2013) 10001-3.

[40] A. Nano, M. P. Gullo, B. Ventura, N. Armaroli, A. Barbieri, R. Ziessel, Panchromatic luminescence from julolidine dyes exhibiting excited state intramolecular proton transfer, Chem. Commun. 51 (2015) 3351-54.

**Highlights:**

- Benzothiazole based molecular species and their corresponding rigidified derivatives with Boron(III) are synthesised.
- The rigidified derivatives are characterised by the locked excited state intramolecular proton transfer based emission behaviour.
- Using binary combination of the molecular species with the complimentary color lights, nearly white light emission, both in solution as well as solid state are obtained.
- The CIE coordinates in solution and in solid states are : x = 0.35753, y = 0.3315 and x = 0.34753, y = 0.32062) respectively.

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