



Room temperature phosphorescence from heavy atom free benzophenone boronic ester derivatives

SWADHIN GARAIN, SUMAN KUILA, ARNAB SINHABABU and SUBI J GEORGE*

New Chemistry Unit and School of Advanced Materials, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore 560064, India

*Author for correspondence (george@jncasr.ac.in; subijg@gmail.com)

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Abstract. Two new boronic ester conjugated benzophenone derivatives are reported, which exhibit visible afterglow phosphorescence under ambient conditions and solution-processable thin films. The carbonyl group and pinacol moiety in the molecular design play a crucial role to achieve good phosphorescence efficiency in air.

Keywords. Phosphorescence; benzophenone; afterglow.

1. Introduction

Room temperature phosphorescence (RTP) from purely organic chromophores has recently received much attention as a promising alternative to expensive and heavy metal-based inorganic phosphors [1–4]. However, design of such molecules has been a challenging task, as most of the organic phosphors suffer low quantum yields at room temperature due to poor inter-system crossing efficiency and high susceptibility toward vibrational as well as oxygen-mediated triplet quenching [5,6]. As a result, organic phosphors with high quantum yield are obtained only in crystalline state, which minimizes the non-radiative quenching of triplet excitons and oxygen diffusion [7–13]. In this context design of solution-processable RTP phosphors is very important for various applications [14–17] and significant impetus is being given for realizing this under ambient conditions. Recently, amorphous state RTP has been achieved in organic systems by incorporating the organic phosphors either in rigid polymer matrices [18–21] or into cage-like hosts [22,23].

Among various organic RTP phosphors, boronic ester-based derivatives are rarely reported [24–29]. Fukushima and co-workers [26] reported that out-of-plane distortion at the B–C bond of the pinacol moiety helps the mixing of σ and π orbitals which would enhance the inter-system crossing (ISC) process to significantly increase the phosphorescence emission. However, most of boronic ester-based RTP designs, suffer from low quantum yield which limits their applications. In addition, simple molecular design is important for the scalable synthesis for various

applications. Hence, in this paper, we report the synthesis of two simple boronic ester appended benzophenone-based solution-processable phosphors (**BBE1** and **BBE2**) with reasonable phosphorescence quantum yield ($\sim 7\%$) under ambient condition. We envisage that, the present design with the carbonyl group [29–35] along with the pinacol moiety would enhance the ISC efficiency.

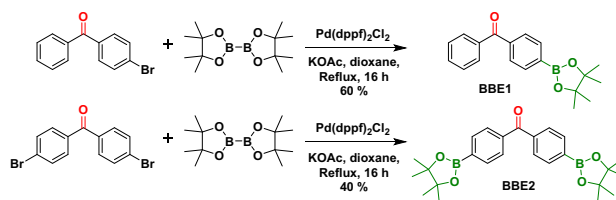
2. Experimental

2.1 Materials

4-Bromo benzophenone, 4,4'-dibromo benzophenone are obtained from Sigma Aldrich. Bis(pinacolato)diboron is obtained from TCI and potassium acetate obtained from SDFCL, India.

2.2 Synthetic procedures of **BBE1** and **BBE2**

BBE1 and **BBE2** are synthesized by Suzuki Miyaura cross-coupling reaction [26] as shown in scheme 1 and the procedures are given below.



Scheme 1. Synthetic scheme of **BBE1** and **BBE2**.

2.2a Synthetic procedure for BBE1: In a 50 ml two-neck round bottom flask, 4-bromo benzophenone (100 mg, 0.382 mmol) was taken and 25 ml dry dioxane was added into it followed by degassing with nitrogen for 10 min [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) ($\text{Pd}(\text{dppf})_2\text{Cl}_2$) (14 mg, 0.02 mmol) and bis(pinacolato)di-boron (106 mg, 0.42 mmol) were added subsequently to the mixture. After 15 min of nitrogen purging, potassium acetate (KOAc) (46 mg, 0.57 mmol) was added and refluxed for 16 h. Dioxane was removed under reduced pressure and column chromatography was performed using chloroform as an eluent to get the pure product as a white solid (71 mg, 60% yield).

^1H NMR (CDCl_3 , 400 MHz), δ (ppm) = 7.92 (*d*, 2H, *J* = 8 Hz), 7.78 (*t*, 4H, *J* = 9.6 Hz), 7.59 (*t*, 1H, *J* = 7.4 Hz), 7.48 (*t*, 2H, *J* = 7.6 Hz), 1.37 (*s*, 12H); ^{13}C NMR (CDCl_3 , 100 MHz), δ (ppm) = 196.9, 139.8, 137.6, 134.6, 132.5, 130.1, 129.0, 128.3, 84.2, 24.9; ^{11}B NMR (CDCl_3 , 600 MHz), δ (ppm) = 29.74. HRMS (ESI): *m/z* calculated 308.1584 [M] $^+$, observed 309.1670 [$\text{M}+\text{H}$] $^+$.

2.2b Synthetic procedure of BBE2: In a 50 ml two-neck round bottom flask 4,4'-dibromo benzophenone (100 mg, 0.294 mmol) was taken and 25 ml dry dioxane was added into it followed by degassing with nitrogen for 10 min. $\text{Pd}(\text{dppf})_2\text{Cl}_2$ (21 mg, 0.03 mmol) and bis(pinacolato)di-boron (164 mg, 0.65 mmol) were added subsequently to the mixture. After 15 min of nitrogen purging, KOAc (87 mg, 0.88 mmol) was added and refluxed for 16 h. Dioxane was removed under reduced pressure and column chromatography was performed using chloroform as an eluent to get the pure product as a pale white solid (51 mg, 40% yield).

^1H NMR (CDCl_3 , 400 MHz), δ (ppm) = 7.91 (*d*, 4H, *J* = 8 Hz), 7.76 (*d*, 4H, *J* = 8 Hz), 1.37 (*s*, 24H); ^{13}C NMR (CDCl_3 , 100 MHz), δ (ppm) = 197.1, 139.7, 134.6, 129.0, 24.9; ^{11}B NMR (CDCl_3 , 600 MHz), δ (ppm) = 29.69. HRMS (ESI): *m/z* calculated 434.2436 [M] $^+$, observed 435.2529 [$\text{M}+\text{H}$] $^+$.

2.3 Protocol for sample preparation

1 mM stock solutions of **BBE1** and **BBE2** were prepared using spectroscopic grade chloroform and all the solution state studies were performed in spectroscopic grade tetrahydrofuran (THF) solvent. Solid state studies were performed as drop-cast film on clean glass slides which are dried under a vacuum for 1 h at room temperature.

2.4 Instruments

2.4a NMR measurements: ^1H , ^{13}C and ^{11}B NMR spectra were recorded on a BRUKER AVANCE-400 and JEOL-600 Fourier transformation spectrometer with 400, 100 and 600 MHz, respectively. The spectra are calibrated with respect to the residual solvent peaks. The chemical shifts are reported in parts per million (ppm) with respect to tetramethylsilane (TMS). Short notations used are, *s* for singlet, *d* for doublet and *t* for triplet.

2.4b Optical measurements: Electronic absorption spectra were recorded on a Perkin Elmer Lambda 900 UV–Vis–NIR spectrometer and emission spectra were recorded on FLS1000 spectrometer, Edinburgh Instruments. Solution state UV–Vis and emission spectra were recorded in a 1 mm path length cuvette. Fluorescence spectra of films were recorded in front-face geometry to avoid self-absorption.

2.4c Lifetime measurements: Fluorescence lifetimes were obtained on a Horiba Delta Flex time-correlated single-photon-counting (TCSPC) instrument. A 373 nm LED laser diode with a pulse repetition rate of 1 MHz was used as the light source. The instrument response function (IRF) was collected by using a scatterer (Ludox AS40 colloidal silica, Sigma-Aldrich). Phosphorescence lifetime ($\lambda_{\text{exc.}} = 330$ nm) and gated emission were measured on FLS1000 spectrometer, Edinburgh Instruments equipped with a micro flash-lamp ($\mu\text{F}2$) set-up. Quantum yields were measured using an integrating sphere in the same instrument.

2.4c HRMS measurements: High-resolution mass spectrometry (HRMS) was carried out using Agilent Technologies 6538 UHD Accurate-Mass Q-TOF LC/MS.

3. Results and discussion

We have synthesized two benzophenone boronic ester derivatives named **BBE1** and **BBE2** (figure 1a) using Suzuki-Miyaura cross-coupling reaction in good yield (scheme 1) and characterized by NMR and HRMS (tables 1 and 2).

First, we have performed detailed photophysical studies of both the derivatives (**BBE1** and **BBE2**) in THF at a concentration of 0.05 mM. **BBE1** and **BBE2** show π - π^* absorption band with a maximum at 255 and 260 nm,

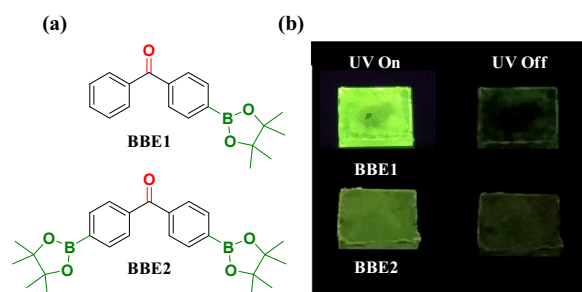


Figure 1. (a) Molecular structures of **BBE1** and **BBE2** and (b) photographs of **BBE1** and **BBE2** under UV light and after switching off the UV light.

Table 1. Fluorescence lifetime of **BBE1** and **BBE2**.

Molecules	τ_1 (ns)	τ_2 (ns)	$\tau_{\text{avg.}}$ (ns)
BBE1	0.53 (22%)	0.86 (78%)	0.8
BBE2	0.39 (48%)	1.57 (52%)	1.0

Table 2. Phosphorescence lifetime and quantum yield of **BBE1** and **BBE2**.

Molecules	τ_1 (ms)	τ_2 (ms)	$\tau_{avg.}$ (ms)	QY (%)
BBE1	6.12 (12%)	28.83 (88%)	26.10	7
BBE2	8.31 (18%)	31.13 (82%)	27.02	2

respectively, and weak absorption band at 300–400 nm region. The weak absorption band could be $n-\pi^*$ in nature (figure 2a and b) [9]. Corresponding emission spectra show the emission maximum at 414 and 448 nm for **BBE1** and **BBE2**, respectively (figure 2a and b). To understand the origin of the emission we monitored excitation spectra at 430 nm, which shows a maximum at 362 nm suggesting that the locally excited emission is originating from the weak $n-\pi^*$ absorption band (figure 2a and b).

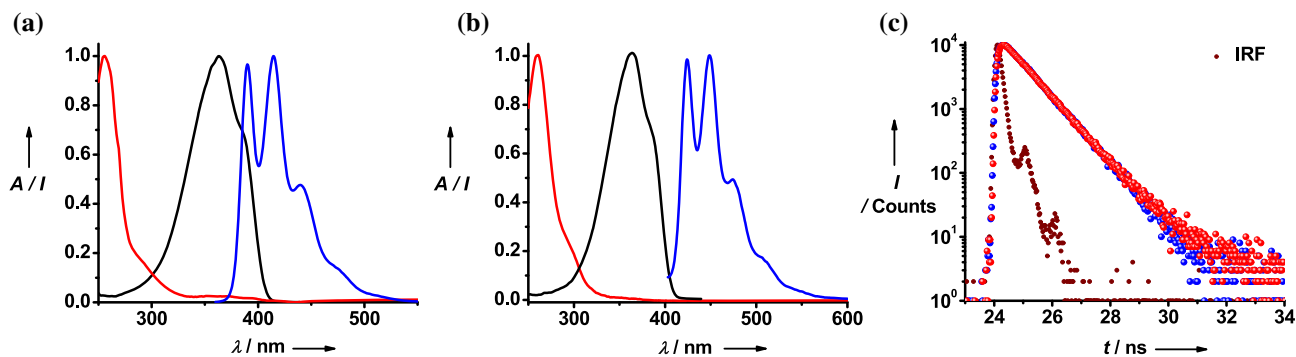


Figure 2. Normalized absorption (red line), emission (blue line) and excitation spectra (black line) of (a) **BBE1** and (b) **BBE2** (concentration = 0.05 mM, $\lambda_{exc.} = 330$ nm, $\lambda_{monitored} = 430$ nm). (c) Lifetime decay profiles of **BBE1** (blue) and **BBE2** (red) ($\lambda_{exc.} = 373$ nm, $\lambda_{collected} = 430$ nm).

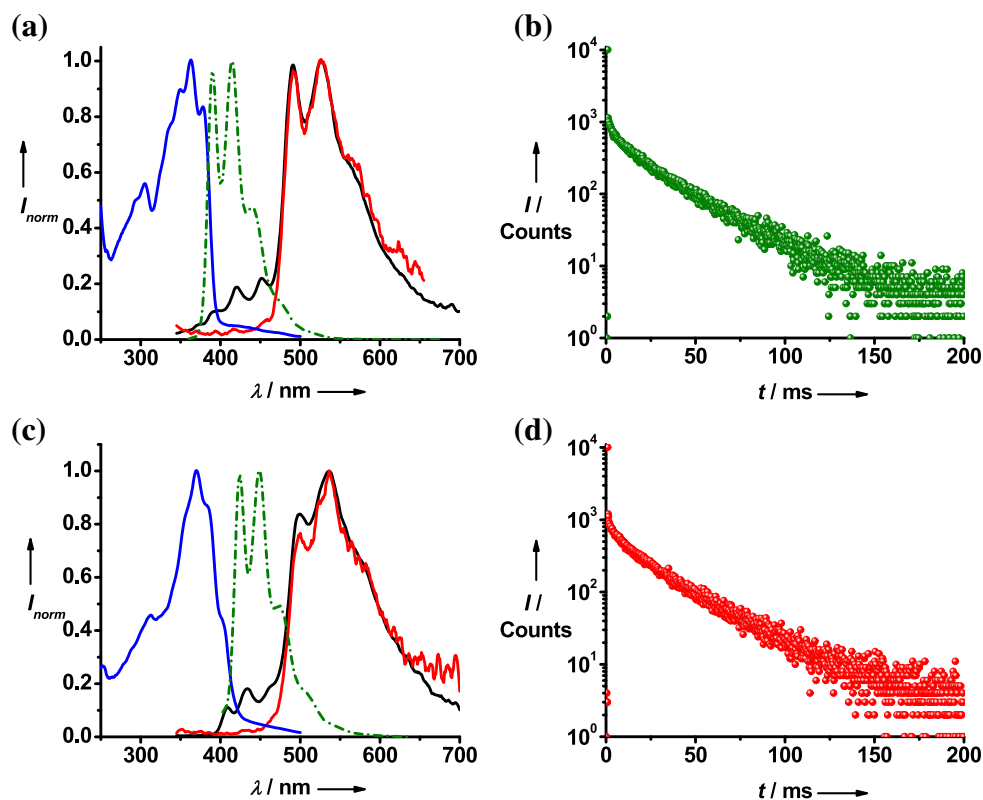


Figure 3. Normalized emission (black line), gated emission (red line), and excitation spectra (blue line) of (a) **BBE1** and (c) **BBE2** ($\lambda_{exc.} = 330$ nm, $\lambda_{monitored} = 520$ nm) in the film along with the emission profile in solution (green dotted line). Lifetime decay plot of (b) **BBE1** and (d) **BBE2** ($\lambda_{exc.} = 330$ nm, $\lambda_{collected} = 520$ nm) in the film state.

Time-resolved fluorescence decay experiments of **BBE1** and **BBE2**, showed an average life time of 0.8 and 1 ns, respectively, clearly indicating the fluorescence nature of the emission in solution state (figure 2c and d). We have not observed any phosphorescence emission as well as long lifetime component at room temperature in solution state which could be due to the non-radiative decay paths of the triplets *via* vibrational or oxygen quenching.

Interestingly, photophysical investigations of the **BBE1** and **BBE2** in the solid state as drop-cast films on a glass slide, showed strikingly different emission characteristics. Upon excitation at 330 nm, a red-shifted emission band with emission maximum at 526 and 536 nm, for **BBE1** and **BBE2**, respectively, was observed compared to the solution state (figure 3a and c). Corresponding excitation spectra monitored at 530 nm shows maximum of 360 and 370 nm, suggesting that the origin of emission is the n to π^* transition for both solution and solid states. To understand the nature of the red-shifted emission in solid state, time-resolved decay experiment was performed. Interestingly, the average lifetime of the red-shifted emission for **BBE1** and **BBE2** was found to be 26 and 27 ms, respectively, with clear afterglow characteristics suggesting the remarkable stabilization of triplets resulting in ambient phosphorescence emission (figure 3b and d). Phosphorescence nature of the emission was further confirmed by the time gated emission spectra (delay time 1 ms), where the fluorescence contribution in the wavelength range of 400–480 nm completely disappeared (figure 3a and c). Phosphorescence quantum yield for **BBE1** and **BBE2** was found to be 7 and 2%, respectively in air. The reason for the lower phosphorescence quantum yield of **BBE2** comparing to **BBE1** is not clear at this point, although we envisage that different molecular packing in the solid state could be the reason for the same.

The vibronic nature of the steady-state emission spectra is suggestive of the locally excited nature of the emission for both fluorescence (400–500 nm) and phosphorescence (460–700 nm) (figure 3). Such spectral feature is in agreement with the previously reported boronic ester-based derivatives [25,26].

4. Conclusion

In conclusion, two benzophenone boronic ester derivatives were synthesized which showed blue fluorescence in solution and ambient green phosphorescence in solid state with clear afterglow emission. More importantly, the synthesis of these novel green boronic ester phosphors could be achieved in a single step with high reaction yields making them ideal for applications. Heavy-atom free and solution-processable ambient phosphors with high life-time and quantum yield have been rarely reported in the literature and we envisage that the derivatives presented here could be

of potential use in sensing, bio-imaging and data encryption.

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