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Highlights	·Solid emission color tuning using a single fluorophore was successfully conducted. ·Bright emission of BODIPY in solid state was achieved by copolymer with styrene as the spacer. ·The emission color changes were induced by intermolecular interaction in the inter-polymer chains.
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Solid emission color tuning of polymers consisting of BODIPY and styrene in various ratios

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ABSTRACT:

Random copolymers (poly(BO_x-*co*-St_y)) consisting of boron dipyrromethene (BODIPY) monomer (BO) and styrene (St) were synthesized to achieve multi-color and efficient emission in the solid state using St as a spacer. The emission color of the resulting copolymers changed from green to red by changing the content of BO from 0.042 to 100 mol%. Fluorescence quantum yield (Φ_f) also increased with the content of St (Φ_f = 0.05-0.88) because the intermolecular distance between the BO fluorophores became longer. The absorption and fluorescence properties of the copolymers in tetrahydrofuran were similar and independent of the compositional ratios, and Φ_f was relatively high (0.65-0.81), which indicates that the intermolecular interaction between BO fluorophores in the same polymer chain is small due to the lack of BO fluorophore aggregation. However, emission color changes in the bulk powder were mainly derived from the intermolecular interaction between BO fluorophores in inter-polymer chains because the polymers were intertwined with each other in the solid state. When the polymers in the solid state were annealed, the emission spectra were red-shifted and Φ_f decreased. It was concluded that the emission color changes of the polymers were mainly induced by intermolecular interaction between BO fluorophores in the inter-polymer chains.

1. Introduction

Boron dipyrromethene (BODIPY; 4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene) derivatives have been applied as fluorescent probes for bio-imaging because of their high fluorescence quantum yield (Φ_f), high molar extinction coefficient, and sharp absorption and fluorescence spectra in solution [1−7]. BODIPY has also attracted much attention for facile color tuning by modification of its substituents. However, in concentrated solution and in the solid state, Φ_f is significantly decreased and the emission spectrum is red-shifted due to π-π stacking and reabsorption of fluorescence derived from high planarity and a small Stokes shift. BODIPY is also reported to have emission bands derived from a single molecule at 550 nm, amorphous aggregation at 600 nm, and *J* dimers at 650 nm [8−10]. Such decrease of Φ_f in the concentrated state is observed in conventional fluorophore. This phenomenon is generally called aggregation-caused quenching (ACQ). The ACQ effect greatly limits practical application in biological systems [11−13]. In contrast, recently, new types of aggregation-induced emission (AIE) fluorophore have been developed [14−23]. In addition, fluorescent polymers with AIE property have attracted much attention on account of well designability, excellent optical properties, and multifunctional potential compared with small organic dyes. Thus, these polymers are expected to the application for a biological field such as tracing biological activity and detecting biological macromolecules [24−28]. To date, the color tuning of BODIPY in the solid state has been investigated using various methods such as molecular modification and the addition of BODIPY with different ratios into poly(methyl methacrylate) (PMMA) film and polystyrene microparticles to control the aggregation state [8,29−31]. Although efficient emission is very rare for BODIPY in the solid state, solid emissive BODIPY has been developed by the incorporation of bulky substituents into a core structure to inhibit the intermolecular π-π stacking. For example, Φ_f in the solid state is 0.09 for general BODIPY with two fluorine atoms connected to boron. On the other hand, Φ_f becomes 0.25 and 0.30 when one fluorine is replaced with a phenyl group or two fluorines are replaced with two phenyl groups, respectively [32]. Bulky triphenylsilylphenyl substituted BODIPY exhibits a relatively high Φ_f ($\Phi_f = 0.25$) [33]. Although various solid emissive BODIPY with AIE character has been developed, Φ_f is at most 0.30 [33−39]. If it is easily possible to change the emission color using a single fluorophore without molecular modification and to create solid emissive materials, then that strategy would be very useful for application to optoelectronic materials for solid-state dye lasers and organic light-emitting diodes [40−45].

Here, we report on the design and fabrication of random copolymers (poly(BO$_x$-*co*-St$_y$)) consisting of BODIPY monomer (BO) and styrene (St) to achieve multi-color and efficient emission in the solid state using St as a spacer (Fig. 1). The optical properties of poly(BO$_x$-*co*-St$_y$) in solution, as a bulk powder, and as a bulk film are also discussed.

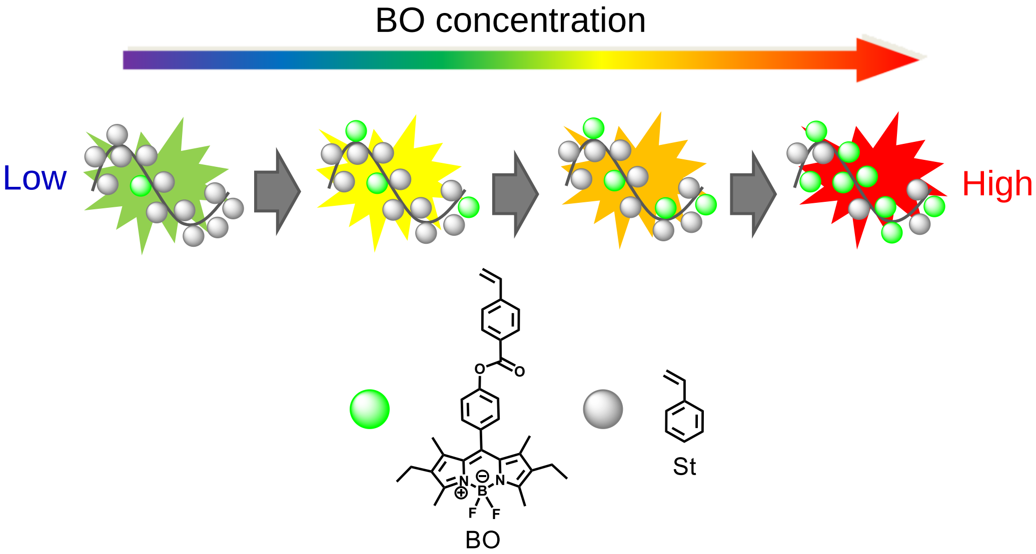


Fig. 1. Emission color changes of polymers consisting of BO and St with various compositions.

2. Experimental section

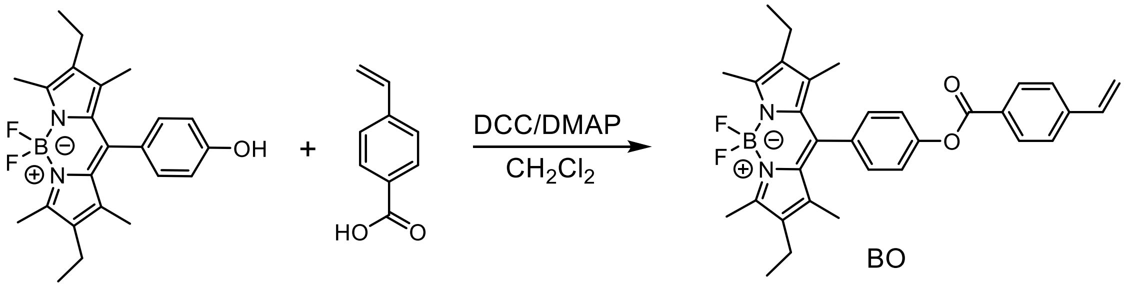
2.1. Measurements

Spectroscopic grade solvents used were and were purified by distillation before use. ^{1}H-NMR (300 MHz) spectra were recorded on a Bruker AV-300N spectrometer with tetramethylsilane (TMS) as an internal standard. Absorption spectra were measured with a JASCO V-560 absorption spectrophotometer. Fluorescence spectra were measured with a JASCO FP-8300 spectrofluorometer. Fluorescence quantum yields were also determined with a JASCO FP-8300 fluorescence spectrometer equipped with a JASCO ILF-835 integrate sphere. Recycling preparative high-performance liquid chromatography (HPLC) was conducted using a JAI LC-908 chromatograph equipped with JAIGEL-1H and 2H columns, and with chloroform as the eluent. Gel-permeation chromatography (GPC) was performed using a Tosoh 8000 series GPC system equipped with TSK-gel columns and tetrahydrofuran (THF) as the eluent at 40 °C. Single-crystal X-ray crystallographic analysis was conducted using a Rigaku AFC/Mercury CCD diffractometer with Mo K_α radiation ($\lambda = 0.71073$ Å) through a graphite monochromator. The crystal structures were solved by a direct method using SIR92 and refined by the full-matrix least-squares method on F^2 with anisotropic displacement parameters for non-hydrogen atoms using SHELXL-2014.

2.2. Materials

All reagents were acquired from Wako Pure Chemical Industries, Sigma-Aldrich, and TCI Chemicals. 2,2'-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol.

2.3. Synthesis of 2,6-diethyl-4,4-difluoro-8-((p-vinylbenzoyloxy)phenyl)-1,3,5,7-dimethyl-4-bora-3a,4a-diaza-s-indacene (BO; Scheme 1)



Scheme 1. Synthesis scheme of BODIPY monomer (BO)

2,6-Diethyl-4,4-difluoro-8-(*p*-hydroxyphenyl)-1,3,5,7-dimethyl-4-bora-3a,4a-diaza-*s*-indacene [46] (400 mg, 1.01 mmol) was dissolved in dichloromethane (70 mL). 4-Dimethylaminopyridine (DMAP) (122 mg, 1.00 mmol), *p*-vinylbenzoic acid (162 mg, 1.09 mmol) and dicyclohexylcarbodiimide (DCC) (206 mg, 1.00 mmol) were added to the solution and stirred for 24 h at room temperature. The reaction mixture was extracted with dichloromethane. The organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by column chromatography on silica gel using *n*-

hexane/dichloromethane (1:2) as the eluent to give 293 mg of BO in 55.4% yield. The ^{1}H-NMR spectrum of the product is shown in Fig. S1. Single crystals were obtained by slow evaporation from a CH_2Cl_2 solution of BO at ambient temperature. The molecular structure and crystallographic data of BO determined by X-ray crystallographic analysis are given in Fig. S2 and Table S1. BO: mp = 226 °C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) $\delta = 0.99$ (t, $J = 7.6$ Hz, CH_3), 1.38 (s, 6H, CH_3), 2.32 (q, $J = 7.6$ Hz, 4H, CH_2), 2.54 (s, 6H, CH_3), 5.45 (d, $J = 11$ Hz, 1H, Vinyl H), 5.94 (d, $J = 18$ Hz, 1H, Vinyl H), 6.81 (dd, $J_1 = 18$ Hz, $J_2 = 11$ Hz, 1H, Vinyl H), 7.36 (s, 4H, Aromatic H), 7.56 (d, $J = 8.4$ Hz, 2H, Aromatic H), 8.19 (d, $J = 8.4$ Hz, 2H, Aromatic H).

2.4. Polymerization

Radical copolymerization of BO and St was conducted in a sealed glass tube under vacuum. The monomer, AIBN, and toluene were placed in a glass tube. The tube was degassed by several freeze-pump-thaw cycles and sealed under vacuum. After polymerization for a prescribed time at 60 °C, the polymers were isolated by recycling preparative HPLC.

3. RESULTS AND DISCUSSION

3.1. Optical properties of BO in solution

The dependence of the emission properties on the concentration of BO monomer in THF was examined to reveal the optical properties of BO without intermolecular interaction. Fig. 2 shows fluorescence spectra for the BO monomer at concentrations of 10^{-6} to 10^{-2} M excited with 480 nm light. The fluorescence spectra were red-shifted ($\Delta\lambda_{em} = 15$ nm) with an increase in the concentration of BO. Φ_f decreased from 0.81 to 0.34 with an increase in the BO concentration from 10^{-6} to 10^{-2} M, as shown in Fig. 2 and Table 1. The difference in the peak-top was as small as 15 nm and Φ_f for the highest concentration (10^{-2} M) was higher than that of general BODIPY in the solid state [32–39]. However, the fluorescence spectra indicate no difference in fluorescence intensity by the concentration of BO monomer at the wavelength above 570 nm. The absorption tail of BO monomer is ca. 570 nm. Thus, this apparent red-shift is ascribed to the re-absorption because of high concentration. These results indicate that significant intermolecular interactions such as π-π stacking or a formation of the dimer were negligible.

The solvent dependence of the optical properties was also examined in various solvents such as ethyl acetate, methanol, *n*-hexane, toluene, THF, and chloroform. No significant differences in the absorption and fluorescence spectra, or in Φ_f were observed with the various solvents, as shown in Fig. S3 and Table S2. These results are very similar to the optical properties of BODIPY in solution reported to date [1−5].

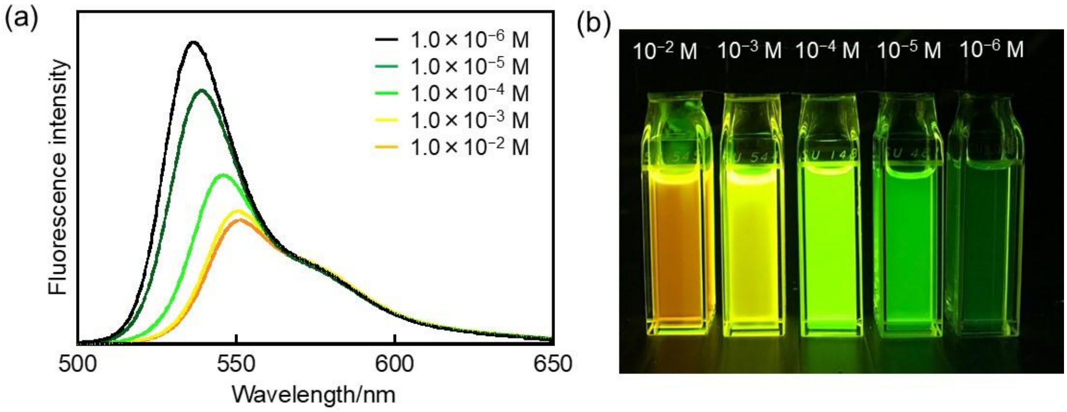


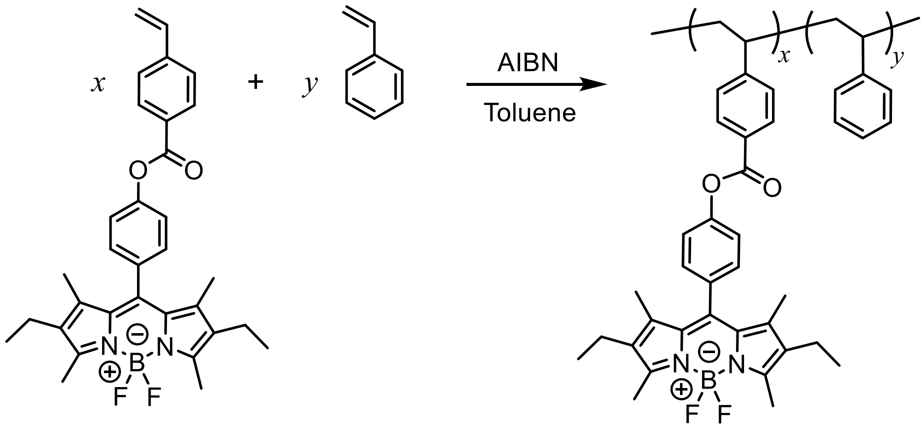
Fig. 2. Fluorescence spectra and optical image of BO monomer in THF. The fluorescence spectra were recorded under excitation with 480 nm light. The optical image was taken under illumination with 365 nm light.

Table 1. Fluorescence properties of various BO concentrations in THF.

[BO] / M	λ_em / nm	Φ_f
1×10^{-6}	537	0.81
1×10^{-5}	539	0.66
1×10^{-4}	546	0.55
1×10^{-3}	551	0.44
1×10^{-2}	552	0.34

3.2. Synthesis and characterization of poly(BO$_x$-co-St$_y$)

Various contents of poly(BO$_x$-*co*-St$_y$) were prepared to control the intermolecular interaction of BODIPY using St as the spacer. Random copolymerization of BO and St was conducted using AIBN as an initiator in toluene at 60 °C for 10 h, as shown in Scheme 2. After the polymerization, the polymers were isolated by recycling preparative HPLC and were reprecipitated in methanol to obtain powder samples. The unreacted BO monomer can be completely removed by this method. Table 2 shows the polymerization conditions, M_n, and M_w/M_n of the resultant polymers. The polymer color in the bulk powder became pale yellow to deep red due to BO, as shown in Fig. S4. The copolymer composition was determined by ^{1}H-NMR spectroscopic analysis of aromatic protons for St and BO. The ^{1}H-NMR spectrum for poly(BO$_x$-*co*-St$_y$) (entry 2) is shown in Fig. S5. The broad peak at 7.85 ppm (indicated by e in Fig. S5) is assigned to *m*-protons of the phenyl group in the styryl group of BO. The sharp peak at 7.30 ppm (f) is assigned to the phenyl protons bound to BODIPY. The peaks at 6.2-6.8 and 6.8-7.2 ppm correspond to the *o*-protons of the styryl groups of BO and St, and the *m*- and *p*-protons of the styryl group of St, respectively. Therefore, the copolymer composition of BO for entry 2 was estimated to be 12 mol%. For poly(BO$_x$-*co*-St$_y$) (entries 3-6), the copolymer compositions were also determined by ^{1}H-NMR spectroscopic analysis, as shown in Fig. S6-S9. These results indicate that various contents of poly(BO$_x$-*co*-St$_y$) were successfully synthesized. Here, we calculated the number of BO and St in a polymer chain using M_n and the feed ratios as shown in Table 2. For poly(BO$_x$-*co*-St$_y$) (entries 2-4), the average number of BO in the polymer chain was more than one. However, for poly(BO$_x$-*co*-St$_y$) (entries 5 and 6), most of the polymer chain did not contain the BO fluorophore, which indicates that the BO fluorophore can exist in isolation not only in solution but also in the polymer.



Scheme 2. Synthesis scheme for poly(BO_x-*co*-St_y).

Table 2. Copolymerization of BO and St in toluene at 60 °C for 10 h.

Entry	[BO] / M	[St] / M	[AIBN] / M	M_n	M_w/M_n	Copolymer composition of BO / mol%	In a polymer chain		
							x	*y*	*y*/*x*
1	0.3	–	0.01	8000	1.59	100	15	0	0
2	0.1	1.5	0.02	17400	1.46	12	13	100	7.5
3	0.05	1.5	0.02	12400	1.74	8.3	7	82	11
4	0.015	1.5	0.02	16700	1.63	1.4	2.1	150	70
5	0.0015	1.5	0.02	10800	1.57	0.25	0.3	103	400
6	0.00015	1.5	0.02	8200	1.57	0.042	0.03	79	2400

3.3. Optical properties of poly(BO_x-co-St_y) in bulk powder and THF.

The optical properties of poly(BO_x-*co*-St_y) bulk powder were examined. Fig. 3 shows the fluorescence spectra and optical images of poly(BO_x-*co*-St_y) with various BO and St contents. Table 3 summarizes the maximum fluorescence wavelength and Φ_f. The emission color of the resulting copolymers changed from green to red with the change in the content from 0.042 (entry 6) to 100 mol% (entry 1), accompanied by a large wavelength shift ($\Delta\lambda_{em}$ = 208 nm). Φ_f also increased (Φ_f = 0.05-0.88) with the St content as the intermolecular distance between BO fluorophores became longer. Compared with the monomer in THF, the differences in the maximum wavelengths and fluorescence quantum yields are very large. This indicates that intermolecular interaction in the solid state and the aggregation of BO fluorophores using St was successfully controlled. For poly(BO_x-*co*-St_y) (entries 1-3), Φ_f was very small because of the re-absorption of fluorescence and formation of the dimer of the BO fluorophores, which is assigned to the emission band around 650 nm [8]. In addition, the homopolymer composed from BO (entry 1) exhibited a new band around 750 nm. The excitation spectra of the homopolymer powder detected at 630 and 750 nm were very similar and were consistent with the diffusion reflectance absorption spectrum, as shown in Fig. S10. This indicates that both fluorescence bands at 650 and 750 nm are attributed to the homopolymer. The band around 750 nm is also indicated that the aggregation level is very high and intermolecular interaction works strongly because the emission band around 550 nm derived from a single BO fluorophore was very weak [8,9]. In contrast, for poly(BO_x-*co*-St_y) (entries 5 and 6), Φ_f was very high because the polymer chain including the BO fluorophore is surrounded by many polymer chains consisting of only St, and the BO fluorophore functions almost as a single fluorophore.

Here, the changes in the emission color are considered to be caused by two factors, which are the intermolecular interaction between BO fluorophores in inter- and intra-polymer chains. The optical properties of poly(BO_x-*co*-St_y) in THF were also measured to confirm the influence of intermolecular interaction in intra-polymer chains. Fig. 4 shows absorption and fluorescence spectra of poly(BO_x-*co*-St_y) excited with 480 nm light. The maximum absorption and fluorescence wavelengths and Φ_f are summarized in Table 3. The spectrum for the homopolymer of BO (entry 1) is red-shifted by 6 nm with respect to those of the other polymers. This indicates that adjacent BO fluorophores in the intra-polymer chain have only small interaction. In contrast, the spectra apart from that for the homopolymer were similar, and Φ_f for all polymers were relatively high (0.65–0.81). These properties were also very similar to those of the BO monomer in THF. It indicates that the intermolecular interaction between BO fluorophores in the same polymer chain is small because the polymers behave as single polymer chains without aggregation in solution.

To elucidate the main interaction that affects the emission property, the poly(BO_x-*co*-St_y) powder was annealed and fluorescence spectra were measured after cooling. Fig. S11 shows fluorescence spectra of poly(BO_x-*co*-St_y) before and after annealing. All of the spectra were red-shifted and the fluorescence intensity was significantly decreased, which indicates that the orientation changed and the intermolecular distance between BO fluorophores was decreased by annealing. It was concluded that the emission color changes of the polymers were mainly induced by intermolecular interactions between BO fluorophores in the inter-polymer chains.

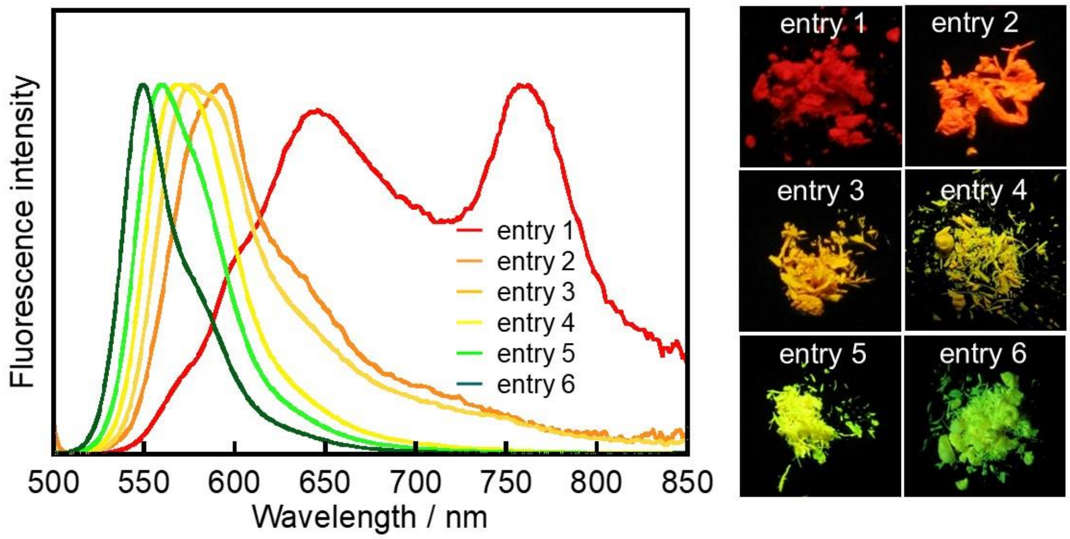


Fig. 3. Fluorescence spectra and optical images of poly(BO$_x$-*co*-St$_y$) in bulk powder. The fluorescence spectra were recorded under excitation with 480 nm light. The optical images were taken under illumination with 365 nm light.

Table 3. Optical properties of poly(BO$_x$-*co*-St$_y$)

Entry	In bulk powder before annealing		In bulk powder after annealing		In THF		In bulk film	
	λ_{em} / nm	Φ_f	λ_{em} / nm	Φ_f	λ_{em} / nm	Φ_f	λ_{em} / nm	Φ_f
1	650, 757	0.05	657, 757	0.03	544	0.70	554, 645, 760	0.07
2	593	0.09	665, 742	0.06	540	0.81	552	0.08
3	576	0.10	664, 750	0.06	540	0.80	553	0.07
4	568	0.24	586, 641	0.16	537	0.83	547	0.35
5	560	0.68	563	0.41	537	0.76	549	0.65
6	549	0.88	552	0.43	538	0.65	545	0.75

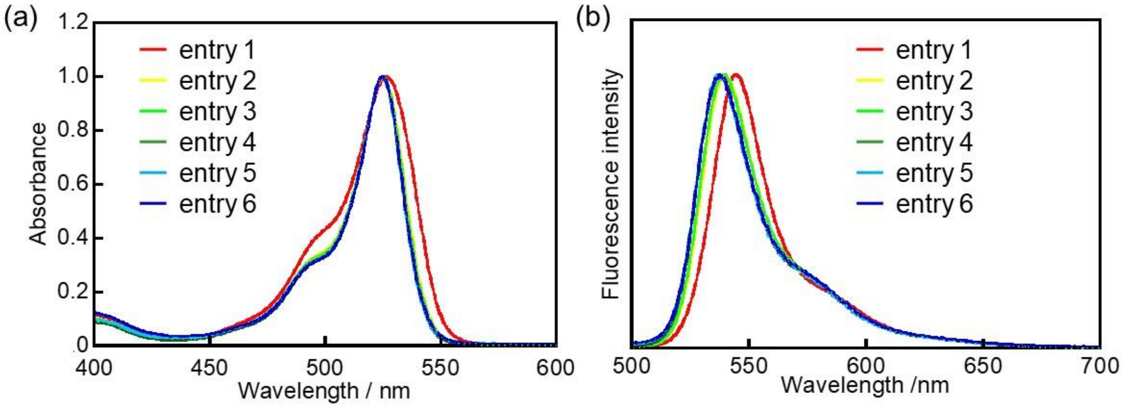


Fig. 4. (a) Absorption and (b) fluorescence spectra of poly(BO$_x$-*co*-St$_y$) in THF excited with 480 nm light.

3.4. Optical properties of poly(BO$_x$-co-St$_y$) in bulk film

To demonstrate the advantage of poly(BO$_x$-*co*-St$_y$) in bulk powder compared with other media, the optical properties of BODIPY in bulk film was also measured. Fig. 5 shows fluorescence spectra for poly(BO$_x$-*co*-St$_y$) in a bulk film excited with 480 nm light. The maximum fluorescence wavelengths and Φ_f are also summarized in Table 3. The film samples were prepared by drop-casting and drying a THF solution of poly(BO$_x$-*co*-St$_y$). Overall, the spectra were blue-shifted compared with the bulk powder and the difference in the peak-tops between each sample became smaller. The polymers (entries 5 and 6) also exhibited high Φ_f (0.65 and 0.75). The emission band of the polymer (entry 1) was similar to that of the bulk powder, although the peak around 550 nm was larger than that for the bulk powder, which indicates that the BO fluorophore works partly as a single molecule. The emission properties were dependent on the level of intermolecular interaction between the inter-polymer chains; therefore, there is interaction in the bulk film and the distance between inter-polymer chains become shorter than that in THF. Thus, the environment of polymer chains in the bulk film is in an intermediate position between that of the solution and the bulk powder. A polymer film prepared from just the addition of BO fluorophore into poly(St) was also examined. The film samples were similarly prepared by drop-casting and drying of a THF solution consisting of BO and poly(St). Fig. S11 shows fluorescence spectra of the mixture of BO and poly(St) in bulk film excited with 480 nm light. The maximum fluorescence wavelengths and Φ_f are summarized in Table S3. *Φ*f increased with the poly(St) concentration, but the peak-tops of the fluorescence spectra and the color observed with the naked eye was not significantly changed. Taking these results into consideration, it is difficult to achieve a distinct multi-color emission with a bulk film because the intermolecular distance of BO cannot be controlled and there may be phase separation between BO and St.

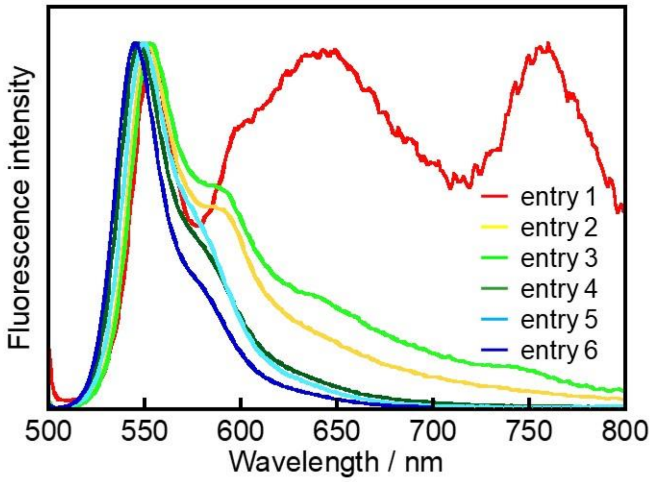


Fig. 5. Fluorescence spectra for poly(BO$_x$-*co*-St$_y$) in bulk films excited with 480 nm light.

4. Conclusion

Poly(BO$_x$-*co*-St$_y$) was synthesized and the emission properties were investigated. Multi-color emissive materials using a single fluorophore were successfully synthesized. Poly(BO$_x$-*co*-St$_y$) (entry 6) exhibits a very high *Φ*f (0.88) which is the highest value among the BODIPY derivatives in the solid state reported to date. The emission color changes of the polymers were demonstrated as being caused by intermolecular interaction between the BO fluorophores in other polymer chains. The width of application could be extended by the addition of other functional groups and materials into this system for the preparation of high-brightness polymers.

Notes

The authors declare no competing financial interests.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.xxxx.xx.xxx.

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