Synthesis of Dual-Emissive Organometallic Complexes Containing Heterogeneous Metal Elements

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ABSTRACT

We present the dual-emissive dye containing heterogeneous organometallic units. The diad ligand composed of two diketonate moieties linked by fluorene was synthesized. By introducing boron and platinum elements, the emissive molecules were obtained. From optical measurements, it was confirmed that the boron and the platinum-containing diads showed the emissions from the charge transfer and the triplet $\pi-\pi^*$ ligand centered transitions, respectively. Next, to observe these fluorescence and phosphorescence properties from the dye molecule, the diad composed of boron and platinum diketonates linked by the fluorene unit were prepared. Finally, the dual emission containing fluorescence from the boron complex and phosphorescence from the platinum complex was simultaneously observed.

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Dual-emissive materials have attracted attention because of their large potential for organic opto and/or electronic devices such as displays and optical chemosensors. For example, by loading the red, green, and blue chromophores into the polymeric matrices, the white-light emissive materials can be obtained.^{1–3} By modulating the feed ratio of each dye, the precise color tuning was accomplished. In these mixture systems, the suppression of the energy transfer is critical for obtaining the desired color and improving device efficiencies. As another instance, the optical sensor based on the fluorescent artificial nucleobase was presented for monitoring the structural alteration of DNA.⁴ The suppression of the molecular motion at the excited state provided the dual emission from the solution, resulting in the color change. Fräser *et al.* synthesized the dual-emissive molecules having both fluorescence and phosphorescence and successfully used them as the ratiometric oxygen sensor in the cells.^{5,6} From the intensity ratio between fluorescence and phosphorescence of the probe molecule, the concentration of the dissolved oxygen can be quantitatively estimated. Thus, the dual-emissive materials, especially single dye molecules, should be feasible in various fields.^{7–11} However, there are still much room to explore the strategy for preparing the dual-emissive molecules. Especially, to apply the dual emission as a practical material in material science as well as in the biotechnology, the establishment of the molecular design for dual-emissive molecules with the bottom up strategy is essential. It is necessary to construct a dual-emissive dye based on the rational design.

A wide variety of elements including main group elements, transition metals and lanthanide ions are capable to form a complex with the β -diketonate ligand.^{12–15} The optical properties of the diketonates are varied by the types of the coordinated elements. In particular, organometallic diketonate complexes

presented various useful characteristics in the polymeric materials according to the recent reports. For instance, it is known that the organoboron-containing compounds showed various unique optical properties.^{16–21} Boron diketonates and their derivatives are also work as emissive dyes with large molar absorption coefficients and high fluorescence quantum yields.^{22–28} It has been demonstrated the modulation of optical properties by changing the complexation ratio of the diketonate ligands on the polymer main-chains.²⁹ Boron diketonates work as a strong electron-acceptor. Significant emissions assigned as the intramolecular charge transfer (CT) states were obtained by increasing the introduction ratio of boron. In general, the CT state can be stabilized in the polar solvents, resulting in the red shift of the emission band. Based on this property, colorful emissive films were readily prepared from the single polymer structure only by changing the complexation ratio. It is known that the platinum complex with the diketonate ligand can show the strong phosphorescence. Swager *et al.* have reported that platinum diketonates with the expanded π -conjugation through the polymer main-chains showed the bright phosphorescence from a triplet $\pi-\pi^*$ ligand centered (3 LC) transition.³⁰ These materials are applicable for improving the efficiencies of the recent opto and/or electric devices.^{31–39} According to these researches, it can be said that the organometallic diketonate ligands are versatile building blocks for constructing advanced optical materials. However, these organometallic diketonate complexes showed brilliant emissions and smart optical properties usually from the single type of metal element. There are very few studies to evaluate the electronic interaction and optical properties of the diketonate complexes with the heterogeneous metal elements in the single molecule.

Scheme 1. Synthetic schemes of the diketonates compounds^a

^aReagents and conditions: (a) BF_3OEt_2 , dichloromethane, rt, 6 h; (b) Pt dimer, Na_2CO_3 , 2-ethoxyethanol, 100 °C, 24 h; (c) i) Pt dimer, Na_2CO_3 , 2-ethoxyethanol, 100 °C, 24 h, ii) BF_3OEt_2 , dichloromethane, r.t., 6 h.

Herein, we report the synthesis and the dual-emission properties of the dye composed of heterogeneous organometallic compounds. Initially, the optical properties of the dual-core diads with two boron or platinum diketonates linked with the fluorene unit were investigated. The two boron complexes-containing diad provided fluorescence from the intramolecular CT band, and the platinum-containing one showed phosphorescence from ^3LC band. Next, to realize the simultaneous detection of each emission from the different spin multiplicities, the emission of the organometallic compound with boron and platinum diketonates linked with fluorene was evaluated. Accordingly, we obtained dual emission composed of fluorescence from the boron complex moiety and phosphorescence from the platinum complex moiety. The feasible strategy can be presented not only for designing dual-emissive compounds but also for obtaining the multi functions in the single molecule.

The synthetic outline of the complexes is shown in Scheme 1. Ligand **5** and boron diketonate **BFB** were prepared according to our previous work.²⁹ To maintain the solubility of the diads, the 9 position at the center of the fluorene unit was modified with the alkyl chains. On the other hand, we found the steric hindrance of these alkyl chains crucially influenced on the yields in the palladium-catalyzed coupling reactions. When 2-ethylhexyl-substituted fluorene was used, the desired product was hardly obtained. Therefore, we used *n*-octyl groups in the diads. The formation of platinum diketonates was performed from **5** by the reaction with Pt dimer prepared with the Swager's report (Scheme S2).⁴⁰ The boron platinum diketonate **BFP** was obtained via two steps from **5**. The mono-substituted platinum complex was synthesized by treating with the 0.65 equivalent of Pt dimer. Subsequently, excess $\text{BF}_3\cdot\text{Et}_2\text{O}$ solution was added to the mono-substituted complex. When boron complexation was carried out before the platinum introduction, a part of boron complexes were replaced to platinum complexes. The synthesized complexes were characterized by ^1H , ^{13}C , and ^{11}B NMR spectroscopies and mass measurements. Finally, we concluded that all products possessed the desired structures with enough purity for the optical measurements.

Figure 1. UV-vis spectra of (a) **BFB**, (b) **PFP** and (c) **BFP** in seven types of organic solvents (1.0×10^{-5} M). **Figure 2.** PL spectra of (a) **BFB**, (b) **PFP** and (c) **BFP** in seven organic solvents (1.0×10^{-5} M) with the excitation light at the wavelength of the absorption maxima.

To investigate the electronic structures of the synthesized complexes at the ground state, UV-vis absorption spectra were monitored in seven organic solvents (Figure 1). The results are summarized in Table 1. The largest absorption bands with the peaks at 460 nm and 370 nm assigned to the $\pi\text{-}\pi^*$ transitions at each complex were observed from **BFB** and **PFP** in all organic solvents, respectively. **BFP** showed significant absorption bands with the peaks around 440 nm and 380 nm. The shape of the spectrum of **BFP** can be explained simply by mixing **BFB** and **PFP**. These data suggest that the electronic interaction between boron and platinum diketonates could be small. In other words, the optical properties of each complex could be intrinsically preserved by the center fluorene unit. The solvent effects were slightly observed from the spectra. These data mean that the perturbation of the electronic structures by the solvent molecules such as coordination or protonation should hardly occur.

The electronic structures of the diketonates at the excited states were evaluated. Initially, the emission behavior of **BFB**

Table 1. Photophysical properties of the diketonates in various kinds of solvents

Compound	BFB			PFP			BFP		
	Φ_{PL}^a	$\lambda_{Abs,max}^b$ (nm)	$\lambda_{PL,max}^c$ (nm)	Φ_{PL}^a	$\lambda_{Abs,max}^b$ (nm)	$\lambda_{PL,max}^c$ (nm)	Φ_{PL}^a	$\lambda_{Abs,max}^b$ (nm)	$\lambda_{PL,max}^c$ (nm)
chloroform	0.78	474	529	0.04	374	538	0.07	381, 432	533
THF	0.61	472	531	0.01	380	538	0.04	383, 426	525
dichloromethane	0.59	474	557	0.05	376	539	0.06	381, 431	540
DMF	0.01	483	588	< 0.01	380	539	0.01	385, 437	573
ethanol	0.10	471	560	0.01	377	538	0.02	381, 428	541
acetonitrile	0.01	473	597	0.01	373	537	0.01	380, 430	541, 579
methanol	0.03	471	574	< 0.01	374	535	0.01	381, 429	544

^aAbsolute quantum yield.^bMeasured in the solution (1.0×10^{-5} M).^cMeasured in the solution (1.0×10^{-5} M) with the excitation light at the maximum peak wavelength of absorption.**Table 2.** Stokes shift and life time of the diketonates in various kinds of solvents

Compound	BFB		PFP		BFP	
	Stokes shift (cm ⁻¹)	τ (ns) ^a	Stokes shift (cm ⁻¹)	τ (ns) ^a	Stokes shift (cm ⁻¹)	τ (ns) ^a
chloroform	2190	1.78	8150	426	1.96, 308 ^b	
THF	2350	1.70	7730	12.6 (17%), 31.7 (83%)	1.70 (88%), 3.11 (12%) 161 (17%) ^b , 353 (83%) ^b	
dichloromethane	3140	1.96	8040	508	2.06 190 (23%) ^b , 342 (77%) ^b	
DMF	3670	0.105 (7%), 0.999 (93%)	7760	0.434 (5%) 2.60 (21%), 6.89 (74%)	0.619 (17%), 1.77 (74%) 6.70 (9%)	
ethanol	3370	0.315 (20%), 1.08 (80%)	7940	14.8 (22%), 35.5 (78%)	1.76 (77%), 20.4 (23%)	
acetonitrile	4390	0.100 (3%), 0.836 (97%)	8190	27.2 (27%), 54.1 (73%)	0.144 (56%), 29.8 (44%)	
methanol	3809	0.757 (45%), 3.10 (55%)	8050	1.72 (16%), 16.2 (84%)	0.967 (83%), 10.7 (17%)	

^aMeasured in the solution, excited at 375 nm (1.0×10^{-5} M) and monitored at each emission maximum wavelength.^bObserved in the longer delay time regions.

was examined (Figure 2a). The PL spectra of **BFB** were measured in chloroform, THF, dichloromethane, DMF, ethanol, acetonitrile, and methanol with the excitation light at the peaks determined from absorption spectra (Table 2). As presented in the previous report, the optical property of **BFB** corresponded to the typical behavior as a CT emission.²⁹ The bathochromic shift and the decreases of the emission intensity were observed by increasing solvent polarity. In chloroform, **BFB** showed strong emission with the peak at 529 nm with high emission efficiency (emission quantum yield, $\Phi = 0.78$). In contrast, in acetonitrile, the emission band was observed in the red-shifted region with the peak at 597 nm with low efficiency ($\Phi = 0.01$). According to the Lippert–Mataga plots prepared from **BFB**, the linear relationship between the solvent polarity and the Stokes shifts was obtained (Figure 3a). The lifetime of **BFB** was about 1–3 ns in each solvent. These changes are the typical behavior as the fluorescence emission from the CT band.

The emission mechanism of **PFP** was investigated. **PFP** exhibited emission bands with the peaks around 540 nm in all organic solvents (Figures 2b). In particular, the significant peak shifts of the emission bands were less observed. Indeed, the less solvent effect was reflected in Lippert–Mataga plots (Figure 3b). The much longer lifetime (426 ns) was observed in chloroform comparing to that of **BFB**. This result indicates that the emission should be phosphorescence. In addition, the significant changes were observed from the PL spectra at 77 K in the glassy state (Figure 4). It is known that the metal-to-ligand CT-based transitions should be critically influenced from the solvent molecules because of large reorganization energies in the polar solvents or rigid media.⁴¹ These results indicate that the emission of **PFP** should be derived from the ³LC transition. Similarly to the Swager's system, energy level of the ³LC state could be lowered comparing to that of the ³CT state by extending the conjugation of diketonate with the fluorene units, leading to the phosphorescence from the ³LC transition.⁴⁰

Finally, we evaluated the optical properties of **BFP**. Notably, the PL spectrum of **BFP** in acetonitrile exhibited two peaks at 541 nm and 579 nm (Figure 2). This result clearly indicates that

Figure 3. Lippert–Mataga plots of (a) **BFB** and (b) **PFP**. The protocols were shown in the Supporting Information. **Figure 4.** PL spectra of **PFP** in THF at room temperature (gray line) and in 2-methyl THF at 77 K (black line).

BFP is the dual-emissive dye. To assign each emission band, we analyzed the optical properties. In contrast to **PFP**, the shape of the emission spectrum of **BFP** seemed to be affected by solvent polarity in the excited states. Although the two peaks were obtained in acetonitrile, the spectrum showed a single peak at 533 nm in chloroform. From the lifetime measurements, it is revealed that the emission of **BFP** mainly involves two elements with both of short (1.96 ns) attributable to the fluorescence and long life times (308 ns) attributed to the phosphorescence. The emissions of **BFB** and **PFP** in chloroform were located at near wavelength region, at 529 nm and 538 nm, respectively. On the

Figure 5. PL spectra of **BFP** in THF at room temperature after argon (gray line) or oxygen (black line) bubbling.

other hand, **BFB** and **PFP** showed the emission bands at 597 nm and 537 nm in acetonitrile, respectively. From these results, it can be summarized that **BFP** has dual emission properties composed of the fluorescence from boron diketonate and the phosphorescence from platinum diketonate. The emission of **BFP** is composed of the overlapping emissions of **BFB** and **PFP**. It should be notified that the phosphorescence emission of **BFP** was hardly influenced by the oxygen concentration (Figure 5). Even after oxygen bubbling through the solution, the magnitude of phosphorescence was maintained. Steric hindrance of alkyl chains at the center fluorene unit could contribute to the preservation of the emissions from both complexes.

We present the synthesis of the diketonate-based diads composed of heterogeneous organometallic complexes. The dual emissions were observed from the synthesized dyes by individually obtaining the emissions from each organometallic complex. This study involves two significant issues: The synthetic procedures for the tandem complexation with boron and platinum elements to the diketonate ligand were established. Because of a wide versatility of boron and platinum diketonates in the optical materials, useful information on the synthesis of the complexes can be provided. Secondly, we present the isolation effect of the fluorene unit in the middle of conjugation system, leading to the dual emissions with fluorescence and phosphorescence. Although the fluorescence quantum yields of boron diketonates were reduced by the introduction of platinum, the mixing spectra with the emissions generated from the different spin multiplicities were obtained. Our findings described here could be applicable for exploiting further combinations with different pairs of metal elements.

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Supporting Information

Synthesis of Dual-Emissive Organometallic Complexes Containing Heterogeneous Metal Elements

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Experimental.

General. ^1H (400 MHz), ^{13}C (100 MHz), and ^{11}B (128 MHz) NMR spectra were recorded on JEOL JNM-EX400 spectrometers. In ^1H NMR spectra and ^{13}C NMR spectra, tetramethylsilane (TMS) was used as an internal standard in CDCl_3 and CD_2Cl_2 . In ^{11}B NMR spectra, $\text{BF}_3\cdot\text{OEt}_2$ (sealed capillary) was used as an external standard. Recyclable preparative high-performance liquid chromatography (HPLC) was carried out on a Japan Analytical Industry Model LC918R (JAIGEL-1H and 2H columns) using chloroform as an eluent. UV-vis absorption spectra were recorded on a Shimadzu UV-3600 spectrophotometer (Shimadzu Corp., Kyoto, Japan). Emission spectra were recorded on a HORIBA JOBIN YVON Fluoromax-4 spectrofluorometer, and absolute quantum yields were determined by the integrating sphere method on the HORIBA JOBIN YVON Fluoromax-4 spectrofluorometer in chloroform (HORIBA, Ltd., Kyoto, Japan). Photoluminescence (PL) lifetime was measured by a Horiba FluoreCube spectrofluorometer system and excitation was carried out at 375nm using UV diode laser (NanoLED 375 nm).

Materials. 2,7-Dibromo-9,9-di-*n*-octylfluorene, Boc_2O (di-*tert*-butyl dicarbonate), DMAP (4-dimethylaminopyridine), $\text{Pd}_2(\text{dba})_3$ (dba = dibenzylideneacetone) and piperidine were purchased

from Tokyo Chemical Industry CO.,LTD. (Tokyo, Japan). 4'-Iodoacetophenone, NaH (sodium hydride) in mineral oil (50~72%), (9,9-dimethyl-fluoren-2-yl)boronic acid, S-Phos (2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl), Cs₂CO₃, 2-phenylpyridine, K₂[PtCl₄] and Na₂CO₃ were purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan). *n*-BuLi in *n*-hexane (1.6 mol/L) was purchased from Kanto Chemical, CO.,INC. (Tokyo, Japan). All solvents were used as a deoxidized grade. All chemicals and solvents were used as received without further purification. The syntheses of the complexes were outlined in Schemes 1 and S1. The diketonate ligand **5** and boron diketonate **BFB** were synthesized according to our previous work (ref #29 in the main text). The synthesis of the ligand was carried out according to Schemes S1 and S2.

Synthesis of 2. Dicarboxylic acid **1** was prepared according to the previous report (Chujo *et al. Macromolecules* **2013**, 46, 2969). The mixture containing **1** (9.2 g, 19.2 mmol) and conc. H₂SO₄ (96%, 2 mL) in methanol (180 mL) was refluxed for 16 h. After neutralization with sat. NaHCO₃*aq.* and evaporation, the residue was dissolved in cyclopentyl methyl ether (CPME), and the organic layer was washed with water, sat. NaHCO₃*aq.* and brine. After drying over Na₂SO₄, volatiles were removed by evaporation. The product **2** was obtained as a white solid (8.9 g, 91%). The authentic sample was purified with recrystallization with THF and methanol. ¹H NMR (CD₂Cl₂, ppm) δ 8.07 (d, *J* = 1.44 Hz, 2H), 8.06 (d, *J* = 1.96 Hz, 2H), 7.83 (d, *J* = 8.56, 2H), 3.93 (s, 6H), 2.12–2.05 (m, 4H), 1.25–0.95 (m, 20H), 0.80 (t, *J* = 7.20 Hz, 6H), 0.58–0.49 (m, 4H). ¹³C NMR (CD₂Cl₂, ppm) δ 167.48, 152.30, 144.89, 130.29, 129.17, 124.55, 120.73, 55.97, 52.41, 40.40, 32.16, 30.25, 29.58, 29.53, 24.13, 22.98, 14.21. HRMS (ESI): calcd for [C₃₃H₄₆O₄+H]⁺: *m/z* 507.3469; found: *m/z* 507.3475

Synthesis of 3. In a round bottom flask with a drop funnel, **2** (3.0 g, 5.9 mmol) and NaH (1.4 mg, 59.3 mmol) were placed under nitrogen atmosphere. The THF solution (50 mL) containing *p*-iodoacetophenone (3.8 mg, 15.4 mmol) was added dropwise at 50 °C over 30 min, and the solution color gradually turned from yellow to orange. Then, the mixture was stirred at 50 °C for 16 h. After quenching the reaction by adding conc. HCl (10%) and removing volatiles by evaporation, the residue was dissolved in CPME, and the organic layer was washed with water, sat. NaHCO₃*aq.* and brine. After drying over Na₂SO₄, volatiles were removed by evaporation. The crude product was purified by the silica gel column chromatography with a mixed eluent containing toluene / *n*-hexane (1/4). Recrystallization with THF and hexane afforded **3** (1.8 g, 32%) as a yellow solid. ¹H NMR (CD₂Cl₂, ppm) δ 17.05 (s, 2H), 8.05 (d, *J* = 6.84 Hz, 4H), 7.91-7.88 (m, 6H), 7.76 (d, *J* = 4.8 Hz, 4H), 6.95 (s, 2H), 2.16–2.12 (m, 4H), 1.20–1.00 (m, 20H), 0.77 (t, *J* = 7.08 Hz, 6H), 0.65–0.55 (m, 4H). ¹³C NMR (CD₂Cl₂, ppm) δ 186.48, 184.85, 152.77, 144.92, 138.44, 135.51, 135.46, 129.00, 127.17, 122.18, 121.13, 100.13, 93.55, 56.21, 40.45, 32.17, 30.26, 29.61, 29.56, 24.21, 22.99, 14.22. HRMS (ESI): calcd for [C₄₇H₅₂I₂O₄+H]⁺: m/z 935.2028; found: m/z 935.2034.

Synthesis of 4. The mixture of **3** (1.5 g, 1.6 mmol), 4,4-dimethylaminopyridine (0.2 g, 1.6 mmol), and di-*t*-butyl dicarbonate (Boc₂O, 3.5 g, 16 mmol) in 1,4-dioxane (150 mL) was stirred at 40 °C for 24 h. After cooling to room temperature, the reaction solution was directly passed through the silica gel swollen with chloroform. After washing with chloroform and subsequently removing solvents, **4** was obtained (1.2 g, 64%) as a yellow solid. ¹H NMR (CD₂Cl₂, ppm) δ 8.02–7.98 (m, 2H), 7.90–7.86 (m, 4H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.80–7.79 (m, 4H), 7.49 (d, *J* = 8.32 Hz, 2H), 7.26 (s, 1H), 7.19 (s, 1H),

2.15–2.05 (m, 4H), 1.53 (s, 18H), 1.25–1.00 (m, 20), 0.78 (t, $J = 7.36$ Hz), 0.65–0.50 (m, 4H). ^{13}C NMR (CD_2Cl_2 , ppm) δ 188.11, 188.08, 187.84, 187.83, 157.75, 157.70, 155.98, 155.93, 153.05, 152.79, 152.57, 152.32, 150.01, 150.01, 149.93, 144.96, 144.85, 143.58, 143.46, 138.53, 138.51, 138.44, 138.41, 183.33, 138.26, 134.04, 134.03, 134.00, 133.76, 129.92, 128.28, 128.22, 127.94, 126.02, 125.99, 123.03, 123.01, 121.47, 121.17, 120.98, 120.82, 120.67, 110.70, 110.67, 109.43, 109.30, 100.80, 100.78, 97.87, 97.85, 84.523, 84.516, 84.46, 84.45, 56.10, 56.05, 56.00, 40.44, 32.10, 30.29, 30.27, 30.25, 29.62, 29.58, 29.56, 29.55, 27.74, 27.72, 24.21, 22.92, 15.43, 14.18. HRMS (ESI): calcd for $[\text{C}_{57}\text{H}_{68}\text{I}_2\text{O}_8+\text{Na}]^+$: m/z 1157.2896; found: m/z 1157.2919.

Synthesis of 5. The mixture containing **4** (650 mg, 0.57 mmol), 9,9-dimethyl-9H-fluorene-2-yl-boronic acid (327 mg, 1.37 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (S-Phos, 9.4 mg, 0.02 mmol), tris(dibenzylideneacetone)dipalladium(0) ($\text{Pd}_2(\text{dba})_3$, 5.2 mg, 6 μmol), and Cs_2CO_3 (1.87 g, 5.73 mmol) in toluene (12 mL) and water (12 mL) was stirred at 80 °C for 16 h. After reaction, an excess amount of cyclopentyl methyl ether was poured to the mixture, and the organic layer was washed with water, sat. $\text{NaHCO}_3\text{aq.}$ and brine. After drying over Na_2SO_4 , volatiles were removed by evaporation. To the solution of the residue in dichloromethane (80 mL), piperidine (113 μL , 1.15 mmol) was added, and then the mixture was stirred at room temperature for 16 h. After neutralization with conc. HCl (10%), the products in dichloromethane were washed with water, sat. $\text{NaHCO}_3\text{aq.}$ and brine. After removing volatiles by evaporation, the crude products were purified with the silica gel column chromatography with a mixed eluent containing *n*-hexane / toluene (1/1). Recrystallization with THF and hexane gave **5** (379 mg) as a yellow solid in 62%

yield. ^1H NMR (CD_2Cl_2 , ppm) δ 17.17 (s, 2H), 8.14 (d, J = 8.30 Hz, 4H), 8.10–8.05 (m, 4H), 7.90 (d, J = 8.32 Hz, 2H), 7.84–7.80 (m, 6H), 7.78–7.71 (m, 4H), 7.66 (dd, J_1 = 7.84, J_2 = 1.96 Hz, 2H), 7.48–7.45 (m, 2H), 7.37–7.31 (m, 4H), 7.04 (s, 2H), 2.18–2.10 (m, 4H), 1.52 (s, 12H), 1.21–0.96 (m, 20H), 0.76 (t, J = 6.88 Hz, 6H), 0.62–0.54 (m, 4H). ^{13}C NMR (CD_2Cl_2 , ppm) δ 186.23, 185.48, 155.01, 154.54, 152.79, 146.03, 144.85, 139.89, 139.34, 138.97, 135.80, 134.57, 128.18, 128.06, 127.70, 127.55, 127.14, 126.73, 123.14, 122.20, 121.92, 121.09, 120.87, 120.65, 93.70, 56.26, 47.44, 40.53, 32.20, 30.30, 29.65, 29.60, 27.41, 24.27, 23.02, 14.23. HRMS (ESI): calcd for $[\text{C}_{77}\text{H}_{79}\text{O}_4+\text{H}]^+$: m/z 1067.5973; found: m/z 1067.5987.

Synthesis of BFB. The mixture containing **5** (100 mg, 0.09 mmol) and $\text{BF}_3\cdot\text{Et}_2\text{O}$ (60 μL , 0.45 mmol) in dichloromethane (20 mL) was stirred at room temperature for 6 h. After quenching the reaction by diluting with dichloromethane, the organic layer was washed with water, sat. $\text{NaHCO}_3\text{aq.}$ and brine. After drying over Na_2SO_4 , the products were suspended onto silica gel. The crude product was purified by the silica gel column chromatography with a mixed eluent containing *n*-hexane / toluene (1/2). The pure **BFB** was obtained (41 mg, 75%) as an orange solid. ^1H NMR (CD_2Cl_2 , ppm) δ 8.50–8.42 (m, 8H), 8.19 (d, J = 8.28 Hz, 2H), 8.02 (d, J = 8.28 Hz, 4H), 7.95–7.89 (4H, m), 7.84–7.78 (6H, m), 7.54–7.50 (2H, m), 7.38–7.31 (4H, m), 2.35–2.28 (4H, m), 1.58 (s, 12H), 1.25–1.00 (m, 20H), 0.80 (t, J = 7.32 Hz, 6H), 0.70–0.58 (m, 4H). ^{13}C NMR ($\text{C}_6\text{D}_6\text{O}$, ppm) δ 183.37, 183.34, 155.57, 155.10, 154.05, 149.16, 147.34, 141.17, 139.42, 139.23, 133.94, 132.01, 130.55, 129.91, 128.61, 128.35, 127.95, 127.43, 124.35, 123.47, 122.56, 122.43, 121.34, 121.16, 94.77, 57.19, 47.82, 40.51, 32.70, 30.84, 30.15, 30.13, 27.40, 24.80, 23.42, 14.32. ^{11}B NMR (CD_2Cl_2 , ppm) δ 0.20. HRMS (ESI): calcd for

$C_{77}H_{76}B_2F_4O_4$: m/z 1162.5894; found: m/z 1162.5901.

Synthesis of Pt dimer. The Pt dimer was synthesized according to Ghedini's report (ref. #40, Scheme S2). In a round-bottom flask, 2-phenylpyridine (1.4 g, 9.3 mmol) was placed under a nitrogen atmosphere, and 2-ethoxyethanol (50 mL) was added. A solution of $K_2[PtCl_4]$ (4.3 g, 10.4 mmol) in degassed water (100 mL) was added dropwise at 80 °C, and then, the mixture was stirred for 6 h. The precipitate was collected by filtration and washed with methanol and water. Pt dimer was obtained (3.06 g, 77%) as a black-green solid. The product was used for the next step directly.

Synthesis of PFP. In a round-bottom flask, **5** (130 mg, 0.122 mmol), Pt dimer (187 mg, 0.244 mmol) and Na_2CO_3 (130 mg, 1.23 mmol) were placed under a nitrogen atmosphere, and 2-ethoxyethanol (80 mL) was added. The mixture was stirred at 100 °C for 24 h. After cooling to room temperature, the product was extracted with CH_2Cl_2 and washed by water. The organic layer was dried over magnesium sulfate and concentrated by a rotary evaporator. The crude product was suspended onto silica gel and purified by the silica gel column chromatography with a mixed eluent containing *n*-hexane/AcOEt (6:1). The desired compound was separated with HPLC in chloroform and precipitated in *n*-hexane. The pure **PFP** was obtained (110 mg, 51%) as a gray solid. 1H NMR

(CD₂Cl₂, ppm) δ 9.20–9.18 (2H, m), 8.28–8.14 (8H, m), 7.94–7.78 (17H, m), 7.71–7.69 (4H, m), 7.54–7.49 (4H, m), 7.38 (4H, dd, J = 8.8, 5.4 Hz), 7.31–7.29 (2H, m), 7.23–7.18 (4H, m), 6.97 (2H, d, J = 2.0 Hz), 2.24–2.23 (4H, m), 1.54 (12H, s), 1.19–1.15 (20H, m), 0.80 (4H, br s), 0.77 (6H, t, J = 6.6 Hz). ¹³C NMR (CD₂Cl₂, ppm) δ 179.52, 179.48, 178.68, 178.67, 178.66, 178.44, 178.39, 177.56, 177.54, 168.04, 167.99, 154.21, 153.73, 151.85, 151.83, 151.82, 151.79, 146.99, 146.87, 144.75, 144.73, 143.73, 143.72, 143.53, 143.07, 142.97, 142.84, 142.74, 139.45, 139.36, 139.06, 139.04, 139.03, 139.01, 138.85, 138.80, 138.70, 138.61, 138.36, 138.34, 138.14, 137.51, 130.53, 130.50, 128.89, 127.35, 127.23, 127.20, 126.98, 126.94, 126.81, 126.34, 126.32, 126.13, 125.90, 125.88, 125.88, 123.38, 123.36, 122.88, 122.40, 121.70, 121.37, 121.26, 121.04, 120.22, 120.17, 120.11, 120.08, 119.89, 118.40, 118.37, 97.13, 55.32, 46.79, 40.16, 40.11, 31.62, 30.05, 30.02, 29.98, 29.17, 26.86, 23.98, 22.45, 13.69. HRMS (APCI): calcd for [C₉₉H₉₂N₂O₄Pt₂+H]⁺: m/z 1762.6404; found: m/z 1762.6414.

Synthesis of BFP. In a round-bottom flask, **5** (70 mg, 0.066 mmol), Pt dimer (31 mg, 0.040 mmol) and Na₂CO₃ (70 mg, 0.66 mmol) were placed under a nitrogen atmosphere, and 2-ethoxyethanol (20 mL) was added. The mixture was stirred at 100 °C for 24 h.

After cooling to room temperature, the product was extracted with CH_2Cl_2 and washed by water. The organic layer was dried over magnesium sulfate and concentrated by a rotary evaporator. The crude product was suspended onto silica gel and purified by the silica gel column chromatography with a mixed eluent containing *n*-hexane/chloroform (1:2). The crude mono Pt complex was obtained (36 mg). $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (6.4 μL , 0.050 mmol) was added to the mixture of the product in dichloromethane (20 mL) at room temperature under a nitrogen atmosphere. After 6 h, the product was extracted with CH_2Cl_2 and washed by water. The organic layer was dried over magnesium sulfate and concentrated by a rotary evaporator. The crude product was separated with HPLC in chloroform and precipitated in *n*-hexane. The pure **BFP** was obtained (18 mg, 19%) as a gray solid. ^1H NMR (CD_2Cl_2) δ 9.13 (1H, br s), 8.24–8.07 (8H, m), 7.85–7.69 (18H, m), 7.46–7.43 (3H, m), 7.30–7.28 (4H, m), 7.23–7.16 (2H, m), 7.09–7.07 (1H, m), 6.90–6.88 (1H, m), 2.15–2.13 (4H, m), 1.48 (12H, s), 1.06 (20H, s), 0.69 (10H, s). ^{13}C NMR (CD_2Cl_2 , ppm) δ 181.64, 181.31, 180.83, 180.76, 178.99, 178.50, 178.36, 178.16, 177.91, 177.85, 177.40, 177.29, 177.05, 176.99, 167.47, 167.39, 153.71, 153.60, 153.22, 153.10, 152.29, 152.14, 152.11, 151.87, 151.78, 151.23, 151.21, 151.18, 146.95, 146.37, 146.25, 144.12, 143.25, 143.16, 143.05, 142.94, 142.46, 142.37, 142.22, 142.14, 140.95, 139.20, 138.83, 138.73, 138.42, 138.37, 138.23, 138.19, 137.70, 137.57, 137.42, 137.21,

136.88, 129.89, 128.67, 128.56, 128.29, 127.92, 127.83, 126.92, 126.72, 126.70, 126.61, 126.36, 126.33, 126.23, 126.17, 125.67, 125.58, 125.46, 125.36, 125.24, 122.76, 122.39, 122.24, 121.80, 121.76, 121.08, 120.75, 120.66, 120.42, 119.91, 119.64, 119.51, 119.43, 119.24, 117.78, 117.75, 96.69, 96.51, 93.05, 92.87, 55.10, 54.70, 46.21, 46.15, 44.93, 39.52, 39.33, 31.11, 30.96, 30.94, 29.38, 29.35, 29.31, 29.20, 29.16, 29.02, 28.87, 28.84, 28.50, 28.47, 28.43, 28.40, 28.34, 26.21, 26.14, 23.31, 23.20, 21.79, 21.78, 13.02, 13.01.

^{11}B NMR (CD_2Cl_2 , ppm) δ 1.57. Positive ion MALDI-TOF-MS (Matrix : DIT): m/z 1463.61820; found: m/z 1463.61696.

Lippert–Mataga plots. The Lippert equation:

$$\nu_{\text{fl}} = \nu_{\text{ab}} - \frac{2\Delta f}{hca^3} (\mu_{\text{E}} - \mu_{\text{G}})^2 + \text{const.} \quad (1)$$

where h equals Planck's constant, c equals the velocity of light in a vacuum, a is the Onsager cavity radius, n and ε the refractive index and the dielectric constant of the solvent, ν_{fl} and ν_{ab} the fluorescence and absorption wavelength (expressed in cm^{-1} units), μ_{E} and μ_{G} the dipole moment (expressed in Debye units) in the excited and the ground state, respectively,

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{4n^2 + 2} \quad (2)$$

While the slope is

$$\text{Slope} = -\frac{2\Delta f}{hca^3} (\mu_{\text{E}} - \mu_{\text{G}})^2 \quad (3)$$

Based on the calculation performed above, we can estimate that the excited state of dyes has a larger dipole moment than the ground state.

Scheme S1. Synthetic scheme of the ligand **5**^a

^aReagents and conditions: (a) conc. H_2SO_4 , methanol, reflux, 16 h; (b) *p*-iodoacetophenone, NaH, THF, 50 °C, 16 h; (c) Boc_2O , 2,4-dimethylaminopyridine, 1,4-dioxane, 40 °C, 16 h; (d) i) 9,9-dimethyl-9H-fluorene-2-yl-boronic acid, S-Phos, $\text{Pd}_2(\text{dba})_3$, Cs_2CO_3 , toluene, water, 80 °C, 16 h, ii) piperidine, dichloromethane, r.t., 16 h.

Scheme S2. Synthetic scheme of the Pt dimer^a

^aconditions: 80 °C, 6 h

Graphical Abstract

Synthesis of Dual-Emissive Organometallic
Complexes Containing Heterogeneous Metal
Elements

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Synthesis of Dual-Emissive Organometallic Complexes Containing Heterogeneous Metal Elements

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ABSTRACT

We present the dual-emissive dye containing heterogeneous organometallic units ~~in the single molecule~~. The diad ligand composed of two diketonate moieties linked by fluorene was synthesized. By introducing boron and platinum elements, the emissive molecules were obtained. From optical measurements, it was confirmed that the boron and the platinum-containing diads showed the emissions from the charge transfer and the triplet π - π^* ligand centered transitions, respectively. Next, to observe these fluorescence and phosphorescence properties from the ~~single-dye~~ molecule, the diad composed of boron and platinum diketonates linked by the fluorene unit were prepared. Finally, the dual emission containing fluorescence from the boron complex and phosphorescence from the platinum complex was simultaneously observed.

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Dual-emissive materials have attracted attention because of their large potential for organic opto and/or electronic devices such as displays and optical chemosensors. For example, by loading the red, green, and blue chromophores into the polymeric matrices, the white-light emissive materials can be obtained.^{1–3} By modulating the feed ratio of each dye, the precise color tuning was accomplished. In these mixture systems, the suppression of the energy transfer is critical for obtaining the desired color and improving device efficiencies. As another instance, the optical sensor based on the fluorescent artificial nucleobase was presented for monitoring the structural alteration of DNA.⁴ The suppression of the molecular motion at the excited state provided the dual emission from the solution, resulting in the color change. Fräser *et al.* synthesized the dual-emissive molecules having both fluorescence and phosphorescence and successfully used them as the ratiometric oxygen sensor in the cells.^{5,6} From the intensity ratio between fluorescence and phosphorescence of the probe molecule, the concentration of the dissolved oxygen can be quantitatively estimated. Thus, the dual-emissive materials, especially single dye molecules, should be feasible in various fields.^{7–11} However, there are still much room to explore the strategy for preparing the dual-emissive ~~single~~ molecules. Especially, to apply the dual emission as a practical material in material science as well as in the biotechnology, the establishment of the molecular design for dual-emissive molecules with the bottom up strategy is essential. It is necessary to construct a dual-emissive dye based on the rational design ~~for a single molecule~~.

A wide variety of elements including main group elements, transition metals and lanthanide ions are capable to form a complex with the β -diketonate ligand.^{12–15} The optical properties of the diketonates are varied by the types of the coordinated

elements. In particular, organometallic diketonate complexes presented various useful characteristics in the polymeric materials according to the recent reports. For instance, it is known that the organoboron-containing compounds showed various unique optical properties.^{16–21} Boron diketonates and their derivatives are also work as emissive dyes with large molar absorption coefficients and high fluorescence quantum yields.^{22–28} It has been demonstrated the modulation of optical properties by changing the complexation ratio of the diketonate ligands on the polymer main-chains.²⁹ Boron diketonates work as a strong electron-acceptor. Significant emissions assigned as the intramolecular charge transfer (CT) states were obtained by increasing the introduction ratio of boron. In general, the CT state can be stabilized in the polar solvents, resulting in the red shift of the emission band. ~~Finally~~Based on this property, colorful emissive films were readily prepared from the single polymer structure only by changing the complexation ratio. It is known that the platinum complex with the diketonate ligand can show the strong phosphorescence. Swager *et al.* have reported that platinum diketonates with the expanded π -conjugation through the polymer main-chains showed the bright phosphorescence from a triplet π - π^* ligand centered (3 LC) transition.³⁰ These materials are applicable for improving the efficiencies of the recent opto and/or electric devices.^{31–39} According to these researches, it can be said that the organometallic diketonate ligands are versatile building blocks for constructing advanced optical materials. However, these organometallic diketonate complexes showed brilliant emissions and smart optical properties usually from the single type of molecules~~metal element~~. ~~In particular,~~There are very few studies to evaluate the electronic interaction and optical properties of the diketonate

complexes with the heterogeneous metal elements in the single

Scheme 1. Synthetic schemes of the diketonates compounds^a

^aReagents and conditions: (a) $\text{BF}_3\cdot\text{OEt}_2$, dichloromethane, rt, 6 h; (b) Pt dimer, Na_2CO_3 , 2-ethoxyethanol, 100 °C, 24 h; (c) i) Pt dimer, Na_2CO_3 , 2-ethoxyethanol, 100 °C, 24 h, ii) $\text{BF}_3\cdot\text{OEt}_2$, dichloromethane, r.t., 6 h.

molecule.

Herein, we report the synthesis and the dual-emission properties of the ~~single-molecular-type~~ dye composed of heterogeneous organometallic compounds. Initially, the optical properties of the dual-core diads with two boron or platinum diketonates linked with the fluorene unit were investigated. The two boron complexes-containing diad provided fluorescence from the intramolecular CT band, and the platinum-containing one showed phosphorescence from ^3LC band. Next, to realize the simultaneous detection of each emission from the different spin multiplicities, the emission of the organometallic compound with boron and platinum diketonates linked with fluorene was evaluated. Accordingly, we obtained dual emission composed of fluorescence from the boron complex moiety and phosphorescence from the platinum complex moiety. The feasible strategy can be presented not only for designing dual-emissive compounds but also for obtaining the multi functions in the single-single molecule.

The synthetic outline of the complexes is shown in Scheme 1. Ligand **5** and boron diketonate **BFB** were prepared according to our previous work.²⁹ To maintain the solubility of the diads, the 9 position at the center of the fluorene unit was modified with the alkyl chains. On the other hand, we found the steric hindrance of these alkyl chains crucially influenced on the yields in the palladium-catalyzed coupling reactions. When 2-ethylhexyl-substituted fluorene was used, the desired product was hardly obtained. Therefore, we used *n*-octyl groups in the diads. The formation of platinum diketonates was performed from **5** by the reaction with Pt dimer prepared with the Swager's report (Scheme S2).⁴⁰ The boron platinum diketonate **BFP** was obtained via two steps from **5**. The mono-substituted platinum complex was synthesized by treating with the 0.65 equivalent of Pt dimer. Subsequently, excess $\text{BF}_3\cdot\text{Et}_2\text{O}$ solution was added to the mono-substituted complex. When boron complexation was carried out before the platinum introduction, a part of boron complexes were replaced to platinum complexes. The synthesized complexes were characterized by ^1H , ^{13}C , and ^{11}B NMR spectroscopies and

mass measurements. Finally, we concluded that all products possessed the desired structures with enough purity for the

Figure 1. UV-vis spectra of (a) **BFB**, (b) **PFP** and (c) **BFP** in seven types of organic solvents (1.0×10^{-5} M).

Figure 2. PL spectra of (a) **BFB**, (b) **PFP** and (c) **BFP** in seven organic solvents (1.0×10^{-5} M) with the excitation light at the wavelength of the absorption maxima.

optical measurements.

To investigate the electronic structures of the synthesized complexes at the ground state, UV-vis absorption spectra were monitored in seven organic solvents (Figure 1). The results are summarized in Table 1. The largest absorption bands with the peaks at 460 nm and 370 nm assigned to the $\pi-\pi^*$ transitions at each complex were observed from **BFB** and **PFP** in all organic solvents, respectively. **BFP** showed significant absorption bands with the peaks around 440 nm and 380 nm. The shape of the spectrum of **BFP** can be explained simply by mixing **BFB** and **PFP**. These data suggest that the electronic interaction between boron and platinum diketonates could be small. In other words, the optical properties of each complex could be intrinsically preserved by the center fluorene unit. The solvent effects were slightly observed from the spectra. These data mean that the

perturbation of the electronic structures by the solvent molecules

lowered comparing to that of the ^3CT state by extending the conjugation of diketonate with the fluorene units, leading to the

Table 1. Photophysical properties of the diketonates in various kinds of solvents

Compound	BFB			PFP			BFP		
	Φ_{PL}^a	$\lambda_{\text{Abs,max}}^b$ (nm)	$\lambda_{\text{PL,max}}^c$ (nm)	Φ_{PL}^a	$\lambda_{\text{Abs,max}}^b$ (nm)	$\lambda_{\text{PL,max}}^c$ (nm)	Φ_{PL}^a	$\lambda_{\text{Abs,max}}^b$ (nm)	$\lambda_{\text{PL,max}}^c$ (nm)
chloroform	0.78	474	529	0.04	374	538	0.07	381, 432	533
THF	0.61	472	531	0.01	380	538	0.04	383, 426	525
dichloromethane	0.59	474	557	0.05	376	539	0.06	381, 431	540
DMF	0.01	483	588	< 0.01	380	539	0.01	385, 437	573
ethanol	0.10	471	560	0.01	377	538	0.02	381, 428	541
acetonitrile	0.01	473	597	0.01	373	537	0.01	380, 430	541, 579
methanol	0.03	471	574	< 0.01	374	535	0.01	381, 429	544

^aAbsolute quantum yield.

^bMeasured in the solution (1.0×10^{-5} M).

^cMeasured in the solution (1.0×10^{-5} M) with the excitation light at the maximum peak wavelength of absorption.

Table 2. Stokes shift and life time of the diketonates in various kinds of solvents

Compound	BFB		PFP		BFP	
	Stokes shift (cm^{-1})	τ (ns) ^a	Stokes shift (cm^{-1})	τ (ns) ^a	Stokes shift (cm^{-1})	τ (ns) ^a
chloroform	2190	1.78	8150	426	196, 308 ^b	1.96, 308 ^b
THF	2350	1.70	7730	12.6 (17%), 31.7 (83%)	1.70 (88%), 3.11 (12%)	1.70 (88%), 3.11 (12%)
dichloromethane	3140	1.96	8040	508	161 (17%) ^b , 353 (83%) ^b	161 (17%) ^b , 353 (83%) ^b
DMF	3670	0.105 (7%), 0.999 (93%)	7760	0.434 (5%)	190 (23%) ^b , 342 (77%) ^b	190 (23%) ^b , 342 (77%) ^b
ethanol	3370	0.315 (20%), 1.08 (80%)	7940	2.60 (21%), 6.89 (74%)	0.619 (17%), 1.77 (74%)	0.619 (17%), 1.77 (74%)
acetonitrile	4390	0.100 (3%), 0.836 (97%)	8190	14.8 (22%), 35.5 (78%)	6.70 (9%)	6.70 (9%)
methanol	3809	0.757 (45%), 3.10 (55%)	8050	27.2 (27%), 54.1 (73%)	1.76 (77%), 20.4 (23%)	1.76 (77%), 20.4 (23%)
				1.72 (16%), 16.2 (84%)	0.144 (56%), 29.8 (44%)	0.144 (56%), 29.8 (44%)
					0.967 (83%), 10.7 (17%)	0.967 (83%), 10.7 (17%)

^aMeasured in the solution, excited at 375 nm (1.0×10^{-5} M) and monitored at each emission maximum wavelength.

^bObserved in the longer delay time regions.

such as coordination or protonation should hardly occur.

The electronic structures of the diketonates at the excited states were evaluated. Initially, the emission behavior of **BFB** was examined (Figure 2a). The PL spectra of **BFB** were measured in chloroform, THF, dichloromethane, DMF, ethanol, acetonitrile, and methanol with the excitation light at the peaks determined from absorption spectra (Table 2). As presented in the previous report, the optical property of **BFB** corresponded to the typical behavior as a CT emission.²⁹ The bathochromic shift and the decreases of the emission intensity were observed by increasing solvent polarity. In chloroform, **BFB** showed strong emission with the peak at 529 nm with high emission efficiency (emission quantum yield, $\Phi = 0.78$). In contrast, in acetonitrile, the emission band was observed in the red-shifted region with the peak at 597 nm with low efficiency ($\Phi = 0.01$). According to the Lippert–Mataga plots prepared from **BFB**, the linear relationship between the solvent polarity and the Stokes shifts was obtained (Figure 3a). The lifetime of **BFB** was about 1–3 ns in each solvent. These changes are the typical behavior as the fluorescence emission from the CT band.

The emission mechanism of **PFP** was investigated. **PFP** exhibited emission bands with the peaks around 540 nm in all organic solvents (Figures 2b). In particular, the significant peak shifts of the emission bands were less observed. Indeed, the less solvent effect was reflected in Lippert–Mataga plots (Figure 3b). The much longer lifetime (426 ns) was observed in chloroform comparing to that of **BFB**. This result indicates that the emission should be phosphorescence. In addition, the significant changes were observed from the PL spectra at 77 K in the glassy state (Figure 4). It is known that the metal-to-ligand CT-based transitions should be critically influenced from the solvent molecules because of large reorganization energies in the polar solvents or rigid media.⁴¹ These results indicate that the emission of **PFP** should be derived from the ^3LC transition. Similarly to the Swager’s system, energy level of the ^3LC state could be

Figure 3. Lippert–Mataga plots of (a) **BFB** and (b) **PFP**. The protocols were shown in the Supporting Information.

Figure 4. PL spectra of **PFP** in THF at room temperature (gray line) and in 2-methyl THF at 77 K (black line).

phosphorescence from the ^3LC transition.⁴⁰

Finally, we evaluated the optical properties of **BFP**. Notably, the PL spectrum of **BFP** in acetonitrile exhibited two peaks at 541 nm and 579 nm (Figure 2). This result clearly indicates that **BFP** is the dual-emissive dye. To assign each emission band, we analyzed the optical properties. In contrast to **PFP**, the shape of the emission spectrum of **BFP** seemed to be affected by solvent polarity in the excited states. Although the two peaks were

obtained in 533 nm in revealed that with both a long life time emissions at wavelength other hand, and 537 nm in acetonitrile, respectively. From these results, it can be summarized that BFP has dual emission properties composed of the fluorescence from boron diketonate and the phosphorescence from platinum diketonate. The emission of BFP is composed of the overlapping emissions of BFB and PFP. It should be notified that the phosphorescence emission of BFP was hardly influenced by the oxygen concentration (Figure 5). Even after oxygen bubbling through the solution, the magnitude of phosphorescence was maintained. Steric hindrance of alkyl chains at the center fluorene unit could contribute to the preservation of the emissions from both complexes.

We present the synthesis of the diketonate-based diads composed of heterogeneous organometallic complexes. The dual emissions were observed from the synthesized dyes by individually obtaining the emissions from each organometallic complex. This study involves two significant issues: The synthetic procedures for the tandem complexation with boron and platinum elements to the diketonate ligand were established. Because of a wide versatility of boron and platinum diketonates in the optical materials, useful information on the synthesis of the complexes can be provided. Secondly, we present the isolation effect of the fluorene unit in the middle of conjugation system, leading to the dual emissions with fluorescence and phosphorescence. Although the fluorescence quantum yields of boron diketonates were reduced by the heavy-atom effect introduction of platinum, the mixing spectra with the emissions generated from the different spin multiplicities were obtained. Our findings described here could be applicable for exploiting further combinations with different pairs of metal elements.

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