

Accepted Article

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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.201903408
Angew. Chem. 10.1002/ange.201903408

Link to VoR: <http://dx.doi.org/10.1002/anie.201903408>
<http://dx.doi.org/10.1002/ange.201903408>

Control of Multicolor and White Emissions by Tuning Equilibrium Between Fluorophores, Lewis Acids, and Their Complexes Using Polymers

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Abstract: Multicolor emissive materials consisting of a single luminophore, a Lewis acid, and their complex were developed. The emissive colors can be tuned by changing the concentration of the solution and the ratio of mixed solvents. Various emissive colors in the solid state were observed by mixing the complexes into polymers in different amounts. The color change is due to equilibrium disruption between the single luminophore, Lewis acid, and its complex. White emission was observed by appropriately controlling the equilibrium by changing the amount of the complex in the polymer.

Multicolor emissive compounds are important because such compounds have potential as full-color displays,^[1] cellular imaging,^[2] fluorescent probes/indicators,^[3] and anticounterfeiting coding.^[4] Among them, multicolor emissive materials with a single luminophore have received considerable attention because the stability/reproducibility of the optoelectronic devices can be improved and the time and cost of production can be reduced when compared with traditional methods,^[5] such as luminophores with different mother skeletons^[6,7] and chromophores with different substituent(s).^[8] Multicolor emission from single-component materials is, however, difficult to achieve due to Kasha's rule, whereby the emission colors are mainly determined by the lowest excited state.^[9] Several methods to achieve multicolor emissive materials with a single luminophore are as follows:^[10] (1) control the equilibrium of protolytic reactions of an emissive dye;^[11] (2) control the equilibrium between a luminophore, a cyclic compound, and its complex;^[12] and (3) control the equilibrium between a fluorescent dye, a Lewis acid, and its complex.^[13]

There have been several reports on multicolor emissive compounds with a single luminophore that exhibit emission in the solid state.^[14] Some examples include (i) single luminophore liquid crystals that exhibit brightly tricolored mechanochromic luminescence;^[15] (ii) π -conjugated systems that consist of a flexible and nonplanar π joint and two emissive rigid and planar wings;^[16] and (iii) combinations of π -conjugated molecules and

Lewis acids.^[17]

White emissive materials are also important in lighting devices and display media.^[18] Such materials are generally prepared by mixing two or more luminophores.^[19] Recently, there have been several reports on white emissions achieved, for example, by (I) excited-state intramolecular proton transfer;^[20] (II) self-folded conformation and multistimuli responsiveness;^[21] (III) using mechanosensitive membrane probes that function by bending rather than twisting;^[22] (IV) a single switchable boron chromophore,^[23] and others.^[24]

We report the development of multicolor (including white color) emissive materials in both solution and solid states by tuning the equilibrium between a single fluorescent dye, a Lewis acid, and its complex. The equilibrium was controlled by conditions such as concentration, ratio of mixed solvents, and the doped amounts in the polymers.

We have recently been interested in fluorescent materials with Lewis acid-base interactions.^[25] Equilibrium between the luminophores, Lewis acids, and their complexes exist, especially, in compounds with intermolecular Lewis acid-base interaction. Initially, we investigated a multicolor emission by controlling the equilibrium in the solution state. The multicolor emission was achieved by the superposition of two emissions from the luminophores and the complexes between the luminophores and the Lewis acid.

A 2.0 mM solution of 4,4-bis(diphenylamino)benzophenone (**1**) in toluene exhibited a light blue fluorescence (maximum fluorescence wavelength = 453 nm, $\Phi_F = 0.03$, Figure 1). On the other hand, an approximately 200 nm red shift occurred and red color emission was observed in a 2.0 mM solution of a mixture of ketone **1** and $B(C_6F_5)_3$ (**2**) in toluene (maximum fluorescence wavelength = 667 nm, $\Phi_F = 0.06$, Figure 1).

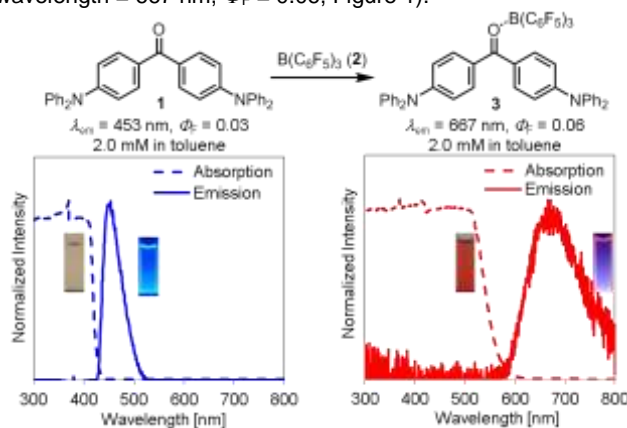


Figure 1. Fluorescent spectra of ketone **1** and complex **3**.

The structure of complex **3** derived from ketone **1** and borane **2** was determined by the following experiments: (1) A proton

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Supporting information and the ORCID identification number for the author of this article can be found under:
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signal at the *ortho*-position of **1** (7.73 ppm) was shifted to the higher field compared with that of **1** (7.35 ppm), most likely due to the effect of the ring current from the pentafluorophenyl group(s) of **2**; (2) a carbon signal of the carbonyl group of **3** (196.4 ppm) was moved to the lower field compared with that of **1** (192.5 ppm); (3) a boron signal of **3** (-2.75 ppm) was shifted to the higher field than that of **1** (-1.05 ppm); and (4) the IR spectrum of **3** corresponded with the simulated IR spectrum of **3**. These results suggested that the Lewis acid-base interaction was formed between the carbonyl group of **1** and the boron atom of **2**, and then complex **3** was formed. In addition, the equilibrium constant was ca. 2800 M^{-1} (for the detail, see the Supporting Information).^[26]

By diluting a 2.0 mM solution of complex **3** (a mixture of ketone **1** and borane **2**) in toluene to 0.10 mM, the emission color changed from red to light blue (Figure 2).^[27] With the change in concentrations, an emission at ca. 667 nm, which is assigned to the emission from **3**, disappeared and an emission at ca. 452 nm, which is assigned as the emission from **1**, appeared. These results show that a large amount of complex **3** formed in 2.0 mM (the degree of the dissociation of **3** calculated by the equilibrium constant was 0.34), but dissociation of complex **3** to ketone **1** and borane **2** occurred in 0.10 mM (the degree of the dissociation of **3** calculated by the equilibrium constant was 0.81). This result suggested that the equilibrium can be moved to **1** and **2** by the dissociation of **3** to increase the total amount of **1**, **2**, and **3** by decreasing the concentration of the solution according to the Le Chatelier's principle.

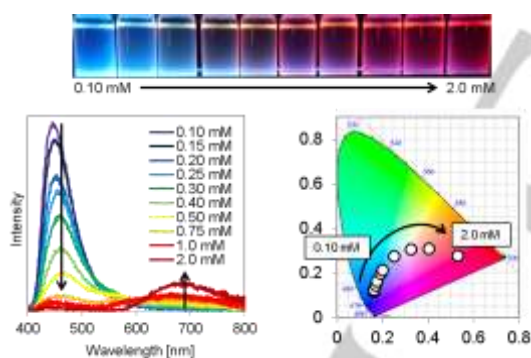


Figure 2. Fluorescent spectra and CIE diagram of a mixture of **1** and **2** in toluene by changing the concentration.

Next, we investigated the emission colors by changing the ratio of solvents (toluene and hexane, 0.10 mM). The emission colors were tuned from blue to red by changing the ratio between toluene and hexane from 10:0 to 0.5:9.5 (Figure 3). These results showed that the equilibrium can be disrupted by changing the ratio of the solvents. One possible explanation of the red shift is the aggregation of **3** by increasing the ratio of hexane because the solubility of **3** decreased by increasing the amount of hexane. However, the aggregates were not observed by DLS (dynamic light scattering). The reason of the phenomenon is not clear yet.

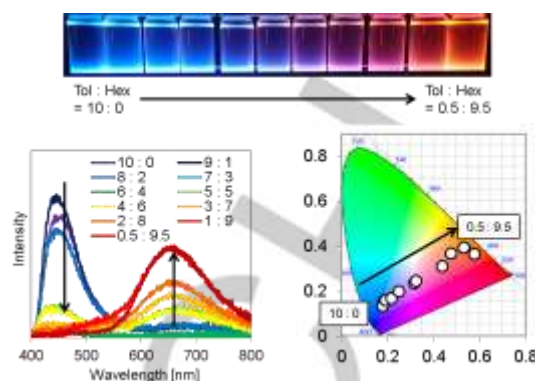


Figure 3. Fluorescent spectra and CIE diagram of a mixture of **1** and **2** in toluene by changing the ratio of mixed solvents.

We succeeded in the observation of white emission by screening the concentration and ratio of solvents. When using toluene (0.75 mM) or a mixed solvent (hexane/toluene/dichloromethane = 5.0:3.5:1.5), the white emissions were observed and the values of the CIE coordinates were (0.32, 0.31) and (0.33, 0.31), respectively (Figure S7).

In contrast to the solution states, it is difficult to develop multicolor emissive materials with a single luminophore in solid state by controlling the equilibrium because the equilibrium must be displaced to the complex side in the solid states. We utilized polymers to avoid the complete formation of complex **3** in the solid states.

Complex **3** between ketone **1** and $\text{B}(\text{C}_6\text{F}_5)_3$ (**2**) showed red color fluorescence in the solid state (maximum fluorescence wavelength = 667 nm, $\Phi_F = 0.06$).^[28] As expected, the red color emission was also observed after removal of the solvents from solutions with each concentration. These results clearly show that the equilibrium moved to the complex side in the solid states.

To avoid the complete formation of complex **3**, we used several polymers. The samples were prepared by removing the solvent from a 1:1 mixture of ketone **1** and borane **2** and a polymer in dichloromethane for each wt% (1.0–20 wt%) of a mixture of **1** and **2** in the polymer. In the case of polystyrene, the fluorescent quantum yield (5.0 wt%, 637 nm, $\Phi_F = 0.21$) was increased higher than that of ketone **1** (484 nm, $\Phi_F = 0.03$) (Figure 4).^[29] The behavior of the color changes depends on the polymers and if they show the Lewis basicity or not (for the details, see the Supporting Information).^[30] In the case of polyvinyl acetate, which has Lewis basicity, a significant red shift was observed by increasing the amount of complex **3** in polyvinyl acetate (Figure 4, Table 1). This is because the relative ratio of the Lewis basic groups in polyvinyl acetate to the Lewis basic moiety of fluorophore **1** decreased and the dissociation of **3** was suppressed by increasing the amount of **3**. In the case of polystyrene, such a red shift did not occur by increasing the amount of complex **3**.

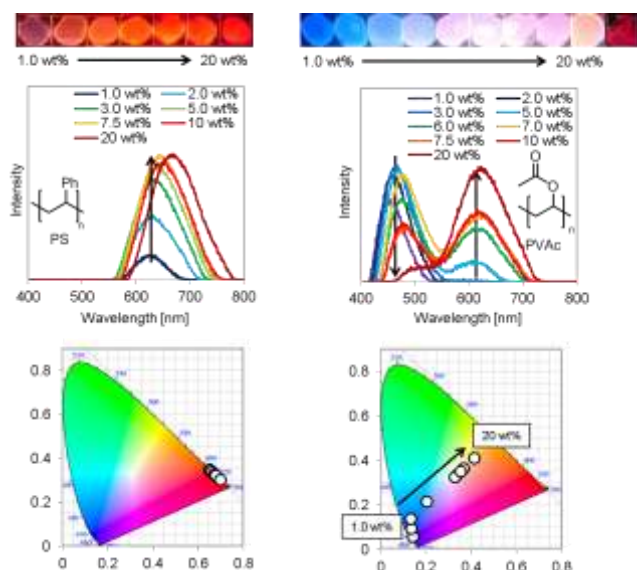


Figure 4. Fluorescent spectra and CIE diagrams of a mixture of **1** and **2** in polystyrene (PS) or polyvinyl acetate (PVAc).

Table 1. Maximum fluorescence wavelengths, ratios of intensities, fluorescent quantum yields, and CIE values of a mixture of **1** and **2** in PVAc.

mix [wt%]	λ_{ex} [nm]	λ_{em} [nm]	I_{620}/I_{470}	Φ_F [nm]	CIE
1.0	380	454	0	0.04	(0.14, 0.06)
2.0	380	455	0	0.05	(0.13, 0.09)
3.0	380	462	0.0040	0.05	(0.13, 0.14)
5.0	380	468, 609	0.16	0.04	(0.20, 0.22)
6.0	380	474, 616	0.65	0.07	(0.34, 0.32)
7.0	380	476, 626	0.62	0.12	(0.33, 0.32)
7.5	380	482, 617	1.4	0.07	(0.42, 0.37)
10	380	478, 616	1.3	0.07	(0.42, 0.35)
20	380	618	34	0.10	(0.57, 0.41)
without polymer	415	690	62	0.06	(0.46, 0.24)

Interestingly, white emission was observed in the case of polyvinyl acetate (Figures 4 and 5, Table 1). We investigated the wt% of a mixture of ketone **1** and $B(C_6F_5)_3$ (**2**) in polyvinyl acetate to achieve white emission. As a result, a sample containing 7.0 wt% of **1** and **2** in polyvinyl acetate exhibited white emission (CIE = (0.33, 0.32), $\Phi_F = 0.12$).^[31] From the fluorescent spectrum, it was revealed that the combination of two emissions (the maximum fluorescent wavelengths = 476 and 630 nm) realized the white emission.

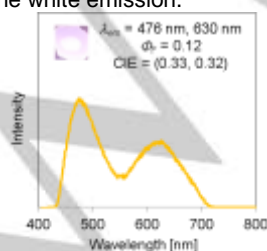


Figure 5. White emission of a mixture of a mixture of **1** and **2** in polyvinyl acetate (PVAc)

The idea that the polymer-doping can tune the emission color as a film was further proved by the use of **4**. A 1:1 mixture of fumaronitrile derivative **4** and borane **2** gave complex **5**, and **5** exhibited orange fluorescence ($\lambda_{em} = 604$ nm, $\Phi_F = 0.38$). By changing the doping amount of a mixture of **4** and **2**, the fluorescent colors changed from light blue to yellow (Figure 6).

In summary, the fluorescent colors in the solution state were tuned from blue to orange by changing the concentration of complex **3** between ketone **1** and borane **2** or the ratio of the mixed solvents. Judging from the fluorescent spectra, these colors were formed by the combination of the fluorescence of **1** and **3**. Although complex **3** exhibited red emission in the solid state, a variety of emissive colors was achieved by doping of a mixture of **1** and **2** into polymers. White emission was also realized by tuning the ratio of the mixed solvent in the solution state and by adjusting the amount of a mixture of **1** and **2** into polyvinyl acetate. A similar phenomenon was observed in another single fluorescent dye, a fumaronitrile derivative.

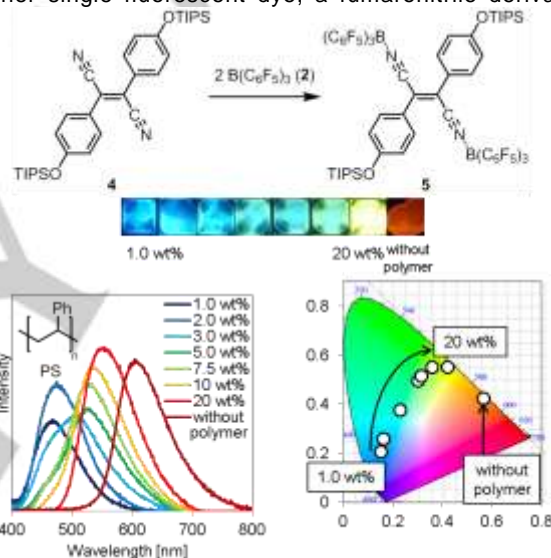


Figure 6. Fluorescent spectra and CIE diagram of a mixture of fumaronitrile derivative **4** and borane **2** in polystyrene (PS).

To the best of our knowledge, this is a novel example of a white color emissive material in which the emissive color can be tuned by doping the 1:1 equilibrium complex between a single fluorescent dye and Lewis acid into polyvinyl acetate in the solid state. We hope that these results will give a good insight into the design of multicolor luminescent materials and become a useful method to prepare such materials.

Acknowledgements

This work was supported in part by Iketani Science and Technology Foundation, The Sumitomo Foundation, The Society of Iodine Science, and A-STEP (VP30218088652) and CREST from JST. We appreciate Prof. Katsuhiko Fujita at Kyushu University for unrestricted access to analytical facilities.

Conflict of interest

The authors declare no conflict of interest.

Keywords: equilibrium • Lewis acid-base interaction • multicolor emission • solid fluorescence • white emission

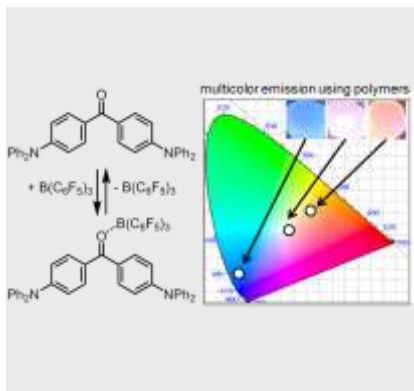
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Entry for the Table of Contents

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Multicolor emissive materials consisting of a single luminophore, a Lewis acid, and their complex were developed. The colors in both the solution and solid states can be tuned by equilibrium disruption between the single luminophore, the Lewis acid, and its complex by controlling the conditions. White emission was observed by appropriately controlling the equilibrium by changing the amount of the complex in the polymer.



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Control of Multicolor and White Emissions by Tuning Equilibrium Between Fluorophores, Lewis Acids, and Their Complexes Using Polymers