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Introduction

Much effort has been devoted to incorporate organic dyes into several matrices such as silica gels derived from sol-gel reactions of alkoxysilanes,1 and polymers such as PMMA2 and PHEMA,3 especially in the field of the development of solid-state dye laser oscillators.4 The incorporation of dyes into these matrices allows the suppression of aggregation between the dyes and the improvement of luminescent properties and photostability.5 Organic-inorganic hybrids have attracted much attention because they can share the characteristics of both organic moieties (flexibility and formability) and inorganic matrices (thermal and mechanical stabilities).5 Optical applications of the dyedoped hybrids have been developed in the field of light-emitting diodes (LEDs),⁶ photochromic materials,⁷ optical sensors,^{8,9} and solid-state dye-lasers.10 By incorporating organic dyes into the matrices homogeneously, the hybrids can possess excellent luminescent properties. On the other hand, the polarity of hybrids is relatively high due to the remaining Si-OH groups, which prevent a high concentration of hydrophobic dyes from being introduced into hybrids. In particular, concentration-quenching

Efficient simultaneous emission from RGB-emitting organoboron dyes incorporated into organic–inorganic hybrids and preparation of white light-emitting materials[†]

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In order to investigate dye-dispersion behaviors in organic–inorganic hybrids, we incorporated RGB lightemitting organoboron dyes (1,3-diketonate BF₂ complex, borondipyrromethene (BODIPY), and boron di(iso)indomethene as blue, green and red light-emitting dyes, respectively) into poly(2-hydroxyethyl methacylate) (PHEMA)–silica hybrids prepared by the microwave-assisted technique. Photoluminescence spectra of two dyes in various concentrations and Stern–Volmer plots indicate that the energy transfer efficiencies between the dyes in the hybrids were lower than that in the solution state, resulting from the suppression of concentration-quenching. Furthermore, we demonstrate the color tuning for preparing white light-emitting hybrids based on simultaneous RGB light-emission of the organoboron dyes. Finally, pure white light-emitting hybrids were obtained by the microwave-assisted *in situ* method.

> often occurs because of non-specific aggregation of the dyes. Therefore, the suppression of stacking between the dyes at the molecular level seems to be important to overcome this problem.

> Recently, we reported the microwave-assisted preparation of methacylate-tethered boron dipyrromethene (BODIPY)-containing PHEMA-silica hybrids using the '*in situ*' method, *i.e.*, the simultaneous sol–gel reaction of alkoxysilanes and radical copolymerization of vinyl monomers.⁵ By using microwave irradiation, the hybrids containing a high concentration of BODIPY were easily obtained so that sol–gel reactions proceeded more quickly than crystallization of BODIPY. In contrast, it was difficult to suppress the phase separation under conventional heating because of rapid crystallization of BOD-IPY. Thus, the microwave irradiation process was proved to be a good tool not only for rapid synthesis of the hybrids (acceleration of reaction) but also for maintenance of homogeneous dispersion of the cohesive molecules such as BODIPY dyes (inhibition of π – π stacking interaction).

Although the emission intensities or quantum yields of dyedoped hybrids have been surveyed in previous reports, there is still much room to evaluate the dispersion behaviors of the dyes at the molecular level in the hybrids. In particular, it is necessary to analyze the electronic interactions of dye molecules in the hybrids for improvement of luminescent properties of the dyes. One of the aims of this study is to clarify the differences of the electronic interaction and molecular distributions of the dyes in the hybrids prepared under microwave irradiation and conventional heating. From the evaluation of the energy transfer efficiencies between two organoboron dyes (boron diketonate 1 and BODIPY 2 illustrated in Scheme 1) incorporated into

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the PHEMA–silica hybrids, we gathered information about the dispersion of the dye molecules. In addition, we demonstrate the color tuning of the hybrids as an application. Finally, we succeeded in obtaining the highly emissive white light-emitting hybrids based on our findings.

Experimental

General

Materials. All reagents were obtained from commercial sources. 2-Hydroxyethyl methacrylate (HEMA) was distilled under reduced pressure. 2,2-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Other reagents were used as received without further purification.

Synthesis of alkoxysilane-modified blue light-emitting 1,3-diketone \cdot BF₂ complex

Alkoxysilane-modified 1,3-diketone \cdot BF₂ complex (1) was synthesized as shown in Scheme 2.



Scheme 2 Synthesis of alkoxysilane-modified organoboron complex 1.

Synthesis of 4-(2-hydroxyethoxy)-benzoic acid methyl ester (4)

Cyclohexanone (240 mL) was added to a mixture of methyl 4hydroxybenzoate (12.2 g, 80 mmol), potassium iodide (6.64 g, 40 mmol), and potassium carbonate (22.1 g, 160 mmol) under nitrogen. To this suspension, 2-chloroethanol (13.4 mL, 200 mmol) was added and then the reaction mixture was stirred at 120-130 °C for 24 h. The resulting suspension was cooled to room temperature and filtered to remove the solids. The yellow-orange filtrate was concentrated in vacuo to yield a mixture containing an orange oil and white solid. Addition of CH₂Cl₂ (180 mL) to the mixture produced a cloudy yellow suspension that was gravity filtered, and the filtrate was concentrated in vacuo. The product was purified by silica gel column chromatography (hexane/EtOAc = 1/1) to afford 7 (9.43) g, 60%) as a white solid. ¹H NMR (CDCl₃, 400 MHz): $\delta = 7.99$ (d, 2H, J = 8.8 Hz, Ar-H), 6.93 (d, 2H, J = 8.8 Hz, Ar-H), 4.14 $(t, 2H, J = 4.5 \text{ Hz}, \text{Ar-OCH}_2-), 3.99 (m, 2H, -CH_2-OH), 3.89 (s, 2H, 2H, 2H)$ 3H, COOCH₃), 2.17 (t, 1H, J = 6.2 Hz, -CH₂-OH) ppm. HRMS (ESI) calcd for $C_{10}H_{13}O_4 [M + H]^+$: m/z 197.0814. Found: m/z197.0810.

Synthesis of 4-methoxy-4'-(2-hydroxyethoxy) dibenzoylmethane (5)

To a suspension of sodium hydride (3.14 g, 131 mmol) in THF (15 mL), a solution of 4'-methoxyacetophenone (6.01 g, 40 mmol) in THF (8 mL) was added dropwise at room temperature under nitrogen. Then, the mixture was heated at 40 °C and a solution of 4 (9.42 g, 48 mmol) was added dropwise. After addition of 4, the mixture was heated at 60 °C and stirred for 10 h. The resulting mixture was cooled at 40 °C, and then toluene (30 mL) and water (40 mL) were added, and pH of the mixture was adjusted to 3 with 75% H₂SO₄. The organic layer was separated, washed with water, and evaporated in vacuo. The resulting solid was purified by recrystallization from 2-propanol to yield a pale yellow solid 5 (4.99 g, 40%). ¹H NMR (CDCl₃, 400 MHz): $\delta = 17.02$ (s, 1H, -(C=O)-CH=C(OH)-), 7.98-7.94 (m, 4H, Ar-H), 7.02-6.96 (m, 4H, Ar-H), 6.73 (s, 1H, -(C=O)-CH= C(OH)-), 4.17 (t, 2H, J = 4.5 Hz, Ar-OC H_2 -), 4.02 (m, 2H, -C H_2 -OH), 3.89 (s, 3H, -OCH₃), 2.01 (s, 1H, -CH₂-OH) ppm. HRMS (ESI) calcd for $C_{18}H_{18}O_5Na [M + Na]^+$: m/z 337.1052. Found: m/z337.1044.

Synthesis of 1,3-diketone · BF₂ complex (6)

BF₃·OEt₂ (0.62 mL, 5.0 mmol) was added to a solution of 5 (1.57 g, 5.0 mmol) in CH₂Cl₂ (200 mL) under nitrogen. After the reaction mixture was stirred under reflux for 1 h, it was cooled at room temperature and the solvent was evaporated *in vacuo*. The resulting solid was purified by recrystallization from acetone/ hexane to afford **6** (0.99 g, 55%) as a yellow solid. ¹H NMR (CDCl₃, 400 MHz): δ = 8.13 (d, 4H, *J* = 8.8 Hz, Ar–*H*), 7.06 (s, 1H, –(C=O)–CH=C(–O)–), 7.02 (d, 4H, *J* = 8.1 Hz, Ar–*H*), 4.21 (t, 2H, *J* = 4.4 Hz, Ar–OCH₂–), 4.03 (m, 2H, –CH₂–OH), 3.93 (s, 3H, –OCH₃), 1.95 (t, 1H, *J* = 6.2 Hz, –CH₂–OH) ppm. HRMS (ESI) calcd for C₁₈H₁₇BF₂O₅Na [M + Na]⁺: *m/z* 385.1035. Found: *m/z* 385.1027.

Synthesis of alkoxysilane-modified 1,3-diketone · BF₂ complex (1)

Dry triethylamine (0.25 mL, 1.8 mmol) was added to a solution of 6 (0.181 g, 0.50 mmol) in THF (10 mL), followed by addition of 3-isocyanatopropyltriethoxysilane (0.39 mL, 1.5 mmol). The solution was stirred under reflux for 12 h, and then cooled at room temperature and the solvent was evaporated in vacuo. The resulting solid was purified by silica gel column chromatography with CHCl₃/acetone (95/5) as an eluent and recrystallization from acetone/hexane to give 1 (0.090 g, 30%). ¹H NMR $(\text{CDCl}_3, 400 \text{ MHz}): \delta = 8.14-8.11 \text{ (m, 4H, Ar-H)}, 7.05-7.01 \text{ (m, })$ 5H, Ar-H, -(C=O)-CH=C(-O)-), 5.05 (s, 1H, -(C=O)-(N-H)-), 4.46 (t, 2H, J = 4.4 Hz, $-(C=O)-OCH_2-$), 4.27 (t, 2H, J = 4.4 Hz, Ar-OCH₂-), 3.93 (s, 3H, -OCH₃), 3.82 (q, 6H, J = 7.1 Hz, Si-OCH₂CH₃), 3.21 (m, 2H, -(C=O)-(N-H)-CH₂-), 1.64 (m, 2H, Si-CH₂CH₂CH₂-), 1.22 (t, 4H, J = 4.4 Hz, Si-OCH₂CH₃), 1.22 (t, 4H, J = 4.4 Hz, Si–CH₂–), ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta =$ 180.9, 180.6, 167.2, 165.3, 156.1, 131.2, 131.1, 124.8, 124.4, 115.0, 114.5, 91.5, 68.8, 62.6, 58.4, 55.7, 43.4, 23.2, 18.2, 7.6 ppm. ¹¹B NMR (CDCl₃, 128 MHz): $\delta = 0.88$ ppm. HRMS (EI) calcd for C₂₈H₃₈BF₂N₂O₅Si [M]⁺: m/z 609.2377. Found: m/z 609.2401. Anal. calcd for C₂₈H₃₈BF₂N₂O₅Si: C, 55.18; H, 6.28; N, 2.30. Found: C, 54.44; H, 6.07; N, 2.35%.

Synthesis of boron di(iso)indomethene dye

Red light-emitting boron di(iso)indomethene dye **3** was synthesized as shown in Scheme 3.

Synthesis of 7

A solution of *o*-hydroxyacetophenone (4.08 g, 30 mmol) and 2methoxybenzhydrazide (7.48 g, 45 mmol) in 1-propanol (40 mL) was stirred at 110 °C for 12 h. After cooling to room temperature, the resulting solid is collected by filtration, washed with 1propanol, and then dried to give 7 (8.53 g, 97%). The obtained 7 was used for the next reaction without purification. ¹H NMR



Scheme 3 Synthesis of boron di(iso)indomethene dye 3.

(CDCl₃, 400 MHz): δ = 12.93 (s, 1H, Ar–O*H*), 10.98 (s, 1H, >C= N–N*H*–(C=O)–), 8.32 (d, 1H, *J* = 6.7 Hz, Ar–*H*), 7.49 (t, 1H, *J* = 7.7 Hz, Ar–*H*), 7.42 (d, 1H, *J* = 7.9 Hz, Ar–*H*), 7.26 (t, 1H, *J* = 7.4 Hz, Ar–*H*), 7.12 (t, 1H, *J* = 7.3 Hz, Ar–*H*), 7.02 (d, 2H, *J* = 7.1 Hz, Ar–*H*), 6.84 (t, 1H, *J* = 7.4 Hz, Ar–*H*), 4.08 (s, 3H, –OC*H*₃), 2.34 (s, 3H, Ar–C(C*H*₃)=N–) ppm. HRMS (APCI) calcd for C₁₆H₁₇N₂O₃ [M + H]⁺: *m*/z 285.1239. Found: *m*/z 285.1240.

Synthesis of 8

Lead tetraacetate (5.47 g, 16.8 mmol) was added to a solution of 7 (3.41 g, 12 mmol) in dry THF (100 mL) in small portions over a period of 5 min. After stirring at room temperature for 3 h, the resulting solid was removed by filtration. The filtrate was concentrated by a rotary evaporator and purified by silica gel column chromatography (CHCl₃) to give **8** (2.86 g, 94%). ¹H NMR (CDCl₃, 400 MHz): δ = 7.66 (d, 2H, *J* = 6.7 Hz, Ar-*H*), 7.51 (m, 3H, Ar-*H*), 7.37 (d, 1H, *J* = 6.7 Hz, Ar-*H*), 7.03 (t, 1H, *J* = 7.5 Hz, Ar-*H*), 6.94 (t, 1H, *J* = 8.5 Hz, Ar-*H*), 3.64 (s, 3H, -OCH₃), 2.49 (s, 3H, Ar-(C=O)-CH₃) ppm. HRMS (APCI) calcd for C₁₆H₁₅O₃ [M + H]⁺: *m*/z 255.1021. Found: *m*/z 255.1021.

Synthesis of di(iso)indomethene ligand (9)

Concentrated NH₄OH (NH₃ content 28–30%, 45 mL) was added to a solution of **8** (2.75 g, 10.8 mmol) in methanol (150 mL) and acetic acid (75 mL). The mixture was stirred at 50 °C for 2 days, and the resulting solid was collected by filtration to yield a crude product. The crude product was purified by silica gel column chromatography with hexane/CHCl₃ = 1/1 as an eluent to give **9** (1.52 g, 62%). ¹H NMR (CDCl₃, 400 MHz): δ = 7.94 (d, 4H, *J* = 5.7 Hz, Ar–*H*), 7.84 (d, 2H, *J* = 7.7 Hz, Ar–*H*), 7.61 (s, 1H, Ar–CH=), 7.35 (m, 4H, Ar–*H*), 7.24 (m, 4H, Ar–*H*), 7.11 (t, 2H, *J* = 7.2 Hz, Ar–*H*), 7.84 (d, 2H, *J* = 8.5 Hz, Ar–*H*), 3.76 (s, 3H, –OC*H*₃) ppm. HRMS (APCI) calcd for C₃₁H₂₅ N₂O₂ [M + H]⁺: *m*/z 457.1916. Found: *m*/z 457.1906.

Synthesis of boron di(iso)indomethene dye (3)

Dry triethylamine (1.71 mL, 12.3 mmol) was added to a solution of 9 (0.562 g, 1.23 mmol) in CH₂Cl₂ (500 mL), followed by addition of $BF_3 \cdot OEt_2$ (3.04 mL, 24.6 mmol). The reaction mixture was stirred at 50 °C for 16 h, and then washed with water. The organic layer was separated, dried over anhydrous magnesium sulfate, and concentrated by a rotary evaporator to give a blue solid. The crude product was purified by silica gel column chromatography (CHCl₃) to afford 3 (0.50 g, 81%) as a metallic red-brown solid. ¹H NMR (CDCl₃, 400 MHz): $\delta = 7.89$ (m, 2H, Ar-*H*), 7.82 (d, 1H, *J* = 2.4 Hz, Ar-*H*), 7.66 (d, 1H, *J* = 7.5 Hz, Ar-H), 7.54 (d, 1H, J = 6.6 Hz, Ar-H), 7.44–7.39 (m, 4H, Ar-H), 7.36-7.33 (m, 2H, Ar-H), 7.27 (m, 1H), 7.17 (m, 2H), 7.08-6.96 (m, 4H), 3.76 and 3.68 (s \times 2, 6H) ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta = 157.7$, 133.8, 132.5, 132.1, 132.0, 131.1, 130.9, 128.6, 127.4, 124.5, 124.4, 123.7, 123.6, 120.4, 120.2, 120.1, 118.8, 115.0, 111.2, 111.0, 55.8, 55.6 ppm. ¹¹B NMR (CDCl₃, 128 MHz): $\delta = 1.37$ (t, J = 37.6, 25.0 Hz) ppm. HRMS (EI) Calcd for $C_{31}H_{23}BF_2N_2O_2[M]^+$: *m*/*z* 504.1821. Found: *m*/*z* 504.1816. Anal. calcd for $C_{31}H_{23}BF_2N_2O_2$: C, 73.83; H, 4.60; N, 5.55. Found: C, 72.01; H, 4.67; N, 5.24%.

Synthesis of green light-emitting BODIPY dyes

The green light-emitting BODIPY dyes with a methacryloyl group **2** were prepared according to the literature.⁵

Preparation of BODIPY-containing polymer-silica hybrid luminescent materials

2-Hydroxyethyl methacrylate (HEMA; 1.0 g, 7.7 mmol) and 2,2'azobis(isobutyronitrile) (AIBN; 2.52 mg) were dissolved in methanol, followed by addition of methyltrimethoxysilane (MeTMOS; 2.0 g) and 0.10 N acetic acid aqueous solution (1.0 mL). The solution was stirred under ambient atmosphere for 3 h to promote hydrolysis of MeTMOS, and 1.0 N ammonium hydroxide (0.10 mL), 1 in 5.0×10^{-3} M THF solution, 2 in 5.0×10^{-3} M THF solution, and 3 in 1.0×10^{-3} M THF solution were added. For example, when the molar ratio of HEMA/1 was 5000/1, 0.308 mL of 1 in 5.0 \times 10⁻³ M THF solution (1.54 \times 10⁻⁶ mol of 1) was added. Then, 2.5 mL of the solution was poured into a polypropylene vessel (20 mL, $\phi = 33 \text{ mm} \times h = 36 \text{ mm}$), and placed into a microwave reactor (Milestone General MicroSYNTH). The microwave (2.45 GHz) was successively irradiated under a nitrogen atmosphere at 30 W for 40 min, 100 W for 10 min, and 300 W for 5 min. For the conventional heating, the solution was put into a 60 °C oven under an argon atmosphere for 24 h.

Measurements

¹H (400 MHz), ¹³C (100 MHz), and ¹¹B (128 MHz) NMR spectra were recorded on a JEOL JNM-EX400 spectrometer. ¹H NMR spectra used tetramethylsilane (TMS) as an internal standard, and ¹¹B NMR spectra were referenced externally to BF₃·OEt₂ (sealed capillary). UV-vis spectra were obtained on a SHIMADZU UV-vis–NIR spectrometer UV-3600. Fluorescence emission spectra were measured on a HORIBA JOBIN YVON FluoroMax-4 fluorescence spectrometer, and absolute luminescent quantum yields were obtained by using an integrating sphere.

Results and discussion

Organoboron dyes such as BF₂ complexes with 1,3-diketones and boron dipyrromethene (BODIPY) exhibit high quantum yields, high molar extinction coefficients, and sharp emission peaks. Herein, boron diketonate, BODIPY, and boron di(iso) indomethene11 were selected as skeletons of blue, green, and red-light emitting dyes, respectively, to be incorporated into the PHEMA-silica hybrids prepared via the microwave-assisted in situ synthesis method. The dyes prepared in this article are shown in Scheme 1. These organoboron dyes would aggregate when incorporated simultaneously into the matrices due to the high planarity of the organoboron dye skeletons. To keep the distances and to suppress energy transferring between the organoboron dyes, we introduced two kinds of substituents (trimethoxysilyl and methacryloyl groups) into the dyes, allowing the dyes to make covalent bonds with silica-polymer matrices, and to be located in the inorganic-organic phase, respectively. In the preparation of the modified dyes, BODIPY dyes with triethoxysilyl groups were not obtained due to high aggregation. Thus, we synthesized a boron diketonate complex tethered with the triethoxysilyl group (blue-emitting dye 1), which is promised to be in inorganic phase. Moreover, to separate the BODIPY and boron di(iso)indomethene dyes, the methacryloyl group was introduced into the BODIPY skeleton (green-emitting dye 2), which could be located in organic phase. For the same reason, no polymerizable group was tethered with the boron di(iso)indomethene dye (red-emitting dye 3), which would be distributed homogeneously in the hybrid. We expected that these different locations and utilization of the microwave process would enhance the dispersibility of the dyes in matrices and suppress energy transferring.

The photophysical properties of organoboron dyes 1, 2, and 3 in THF are shown in Table 1. Dye 1 exhibited an absorption maximum at 410 nm corresponded to a $\pi \rightarrow \pi^*$ transition in the UV-vis absorption spectrum. Upon excitation at the absorption maximum, dye 1 showed the strong blue light emission with the peak at 426 nm. The absorptions of BODIPY dyes 2 and 3 were also characterized by strong $\pi \rightarrow \pi^*$ transition at 520 and 625 nm, and the emission colors were bright green and red, respectively. These organoboron dyes possess large molar absorption coefficients and high quantum yields.12 As shown in Fig. 1, these dyes exhibited sharp absorption and photoluminescence (PL) peaks, and small Stokes shifts (16-28 nm), implying low energy transferring ratios between each dye. Further, the dyes would be located in different surroundings during hybridization due to different substituents such as triethoxysilyl and methacryloyl groups, or no polymerizable group. These chemical

 Table 1
 Spectroscopic data of organoboron dyes^a

Dye	$\lambda_{\max(abs)} [nm]$	ε_{\max}	$\lambda_{\max(em)} [nm]$	$\Phi_{ m F}$
1	410	72 700	426	0.82
2	520	88 500	538	0.72
3	625	98 700	653	0.48

 a 1.0 \times 10 $^{-5}$ M in THF for dyes 1 and 3, in methanol for dye 2.



Fig. 1 Absorption (dashed line) and photoluminescence spectra (solid line) of THF solution of (a) dye **1**, (b) dye **2**, and (c) dye **3**. Concentrations of the dyes are 1.0×10^{-5} M.

modifications could contribute to suppressing energy transferring *via* a Förster mechanism in which the efficiency is significantly dependent on the spectrum overwrap between the donor emission and the acceptor absorption bands.

Organic-inorganic hybrids emitting blue light were prepared by the microwave-assisted in situ method. 2-Hydroxyethyl methacrylate (HEMA) was used as a polymerizable monomer, and methyltrimethoxysilane (MeTMOS) as an alkoxysilane for the formation of silica matrices. To avoid the self-quenching of the fluorophores, dye 1 was added to the reaction solution, hydrolyzed and co-condensed with MeTMOS.5 The molar ratio of HEMA/1 was 5000/1, and the feed ratio of HEMA/MeTMOS was 1/2. Here, AIBN and acetic acid were used as a radical initiator and a catalyst of the sol-gel reaction of MeTMOS, respectively. These reactions were carried out under microwave irradiation at 30 W for 40 min, 100 W for 10 min, and 300 W for 5 min. As shown in Fig. 2, a yellowish and transparent hybrid was obtained by the microwave irradiation. UV-vis and PL spectra of dye 1 in the hybrid and THF solution are illustrated in Fig. 3. The hybrid exhibited absorption maximum at 387 nm, and the relatively sharp PL peak at 440 nm upon excitation with absorption maximum. The PL peak was located on a slightly longer wavelength in comparison with 1 in THF solution (1.0 imes 10^{-5} M). This could be due to the stacking formation under the



Fig. 2 Photographs of (a) appearance and (b) UV irradiation state of BODIPY dye **1**-containing PHEMA–silica hybrids prepared under microwave irradiation. The feed ratio of HEMA/MeTMOS was 1/2. The molar ratio of HEMA/**1** was 5000/1.



Fig. 3 Absorption and photoluminescence spectra of BODIPY dye **1** $(1.0 \times 10^{-5}$ M THF solution, dashed line), and dye **1**-containing PHEMA–silica hybrids (solid line) prepared under microwave irradiation. The feed ratio of HEMA/MeTMOS was 1/2. The molar ratio of HEMA/**1** was 5000/1.

higher concentrations of dye **1** in the hybrid than that in the solution. The apparent concentration of dye **1** in the hybrid was 1.2×10^{-3} M, indicating that microwave irradiation allows incorporation of dye **1** at high concentration into the hybrids. The obtained hybrid showed a high enough absolute luminescence quantum yield of 0.59, while the quantum yield slightly decreased relative to the solution state. This result indicates the enhancement of the dispersion in solid sate of dye **1**.

To investigate the energy transfer efficiency between dyes 1 and 2, we carried out the PL spectroscopic study of dye 1 with different concentrations of dye 2 in THF solution and the PHEMA-silica hybrids prepared by the present microwave technique (Fig. 4). The concentration of dye 1 was fixed at 1.2×10^{-3} M in the hybrids and 1.0×10^{-3} M in the THF solution, respectively. In the solution state, the PL intensity of dye 1 decreased dramatically when more than 0.50 eq. of dye 2 was added (Fig. 4a). On the other hand, in the PHEMA-silica hybrids, the extent of the decrease in the PL intensity of dye 1 was much smaller than that in the solution state (Fig. 4b). When 0.50 eq. of dye 2 was added, the estimated energy transfer



Fig. 4 Photoluminescence spectra of (a) mixtures of 1 and 2 in THF, and (b) PHEMA–silica hybrids doped with 1 and 2. Concentrations of 1 were (a) 1.0×10^{-3} M and (b) 1.2×10^{-3} M.

efficiency between dyes **1** and **2** was 75% in the solution state, and 35% in the hybrids, respectively. These results indicate that the energy transfer efficiency between the incorporated dyes in the hybrids should be suppressed compared to the solution state. This could be attributed to that each dye doped in the hybrid could be isolated by silica matrices, and the long enough distance between each dye is retained in the hybrid, leading to the suppression of the concentration-quenching.

We prepared the Stern-Volmer plots from the results of Fig. 4. The plots of I_0/I versus the concentration of dye 2 in the solution state and in the PHEMA-silica hybrids are shown in Fig. 5, where I and I_0 are the fluorescence intensities of dye 1 in the presence and absence of dye 2, respectively. In the solution state, plots of I_0/I decreased linearly as the concentration of dye 2 increased. This is due to the dynamic quenching derived from the diffusion of the dyes. In the hybrids, a decrease in the intensity was observed when more than 1.0 eq. of dye 2 was added. At the low concentration of dye 2, the slope of the line was quite small. Above 1.0 eq. of dye 2, the slope of the fitting line obtained from the hybrid was almost the same as that from the solution state. In the high concentration range of dye 2, the decrease in PL intensity of dye 1 should cause the static quenching between these dyes due to short distances between them. In the low concentration range, these dyes were embedded in the hybrid, so that the location between each dye in the hybrid could be a far enough distance.

Similar results were found from the same experiment using dyes 2 and 3. The results are presented in Fig. 6 and 7. When 1.0 eq. of dye 3 was added, the energy transfer efficiencies between dyes 2 and 3 were 99% in the solution state and 28% in the hybrid, respectively. It was found that the energy transfer between dyes 2 and 3 was more suppressed in the hybrids as compared to that between dyes 1 and 2. Dyes 2 and 3 are likely to assemble *via* π - π stacking interaction, resulting in the increase of concentration-quenching. Homogeneous dispersion and embedment of these dyes in the hybrids would effectively suppress the concentration-quenching.



Fig. 5 Stern–Volmer plots of (a) mixtures of 1 and 2 in THF solution, and (b) PHEMA–silica hybrids doped with 1 and 2. Concentrations of 1 were (a) 1.0×10^{-3} M and (b) 1.2×10^{-3} M.





(a)

Normalized Intensity

530

580

Fig. 6 Photoluminescence spectra of (a) mixtures of 2 and 3 in THF, and (b) PHEMA–silica hybrids doped with 2 and 3. Concentrations of 2 were (a) 1.0×10^{-3} M and (b) 1.2×10^{-3} M.

In the previous section, it was found that the energy transferring between the two pairs of the dyes embedded in the hybrids was suppressed as compared to the solution state.



Fig. 7 Stern–Volmer plots of (a) mixtures of **2** and **3** in THF solution, and (b) PHEMA–silica hybrids doped with **2** and **3**. Concentrations of **2** were (a) 1.0×10^{-3} M and (b) 1.2×10^{-3} M.

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Herein, we attempted to prepare white light-emitting PHEMAsilica hybrids by incorporating three RGB light-emitting dyes 1 (blue emission), 2 (green emission), and 3 (red emission). In general, it is difficult to control the white light-emission in the case of simultaneous emission from the matrices containing RGB light-emitting dyes. Since the energy transfer between the dyes has to be prohibited, the concentrations of the dyes should be low for obtaining the pure white light emission. According to Fig. 1, it was shown that the overlaps between the emission spectra of dye 1 (dye 2) and the absorption spectra of dye 2 (dye 3) are quite small, suggesting the low energy transfer efficiency between these dyes. In the hybrids, more efficient suppression of the energy transfer can be expected. Furthermore, the microwave-assisted *in situ* preparation method could allow homogeneous dispersion of these dyes.

Initially, we explored the optimum concentration and ratio of RGB dyes 1, 2, and 3 for the preparation of white lightemitting PHEMA-silica hybrids. CIE coordinates of the hybrids with various concentrations of these dyes are shown in Fig. 8. The excitation wavelength was at 387 nm. When the concentrations of the dyes were low (7.7 \times 10^{-8} mol in the reaction solution), the CIE coordinate of the obtained hybrids was (0.32, 0.43). When the concentration of dye 1 increased, the coordinate came near to the white color. High concentration dye 3 led to the shift of the coordinate to the blue region. To obtain white light-emission, the amounts of dyes 1 and 3 in the reaction solution were adjusted to 1.54×10^{-6} mol and 3.08×10^{-7} mol, respectively, and the concentration of dye 2 was optimized. Accordingly, we successfully obtained a white light-emitting hybrid with CIE coordination (0.31, 0.34) when the ratio of these dyes (B/G/R) was 20/15/4. The concentrations of dyes 1, 2, and 3 were 1.2 \times 10 $^{-3}$ M, 9.0 \times 10 $^{-4}$ M, and 2.4 \times 10 $^{-4}$ M, respectively. The appearances under visible and UV light are shown in Fig. 9a and b, respectively. Fig. 10 shows absorption and PL



Fig. 8 CIE diagram of PEMA–silica hybrids containing RGB light-emitting organoboron dyes. The molar ratios of **1/2/3** were (a) 1/0/0, (b) 0/1/0, (c) 0/0/1, (d) 1/1/1, (e) 10/1/1, (f) 10/1/10, (g) 20/10/4, (h) 20/20/4, and (i) 20/15/4, respectively. In the case of (i), the concentrations of dyes **1**, **2**, and **3** were 1.2 × 10^{-3} M, 9.0 × 10^{-4} M, and 2.4 × 10^{-4} M, respectively.

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Fig. 9 Photographs of RGB light-emitting dyes containing PHEMA–silica hybrids prepared under microwave irradiation taken under (a) visible light and (b) UV light.



Fig. 10 Absorption (dashed line) and photoluminescence (solid line) spectra of white light-emitting PHEMA-silica hybrid prepared under microwave irradiation. The concentrations of dyes in the hybrid were 1.2×10^{-3} M for dye **1**, 9.0×10^{-4} M for dye **2**, and 2.4×10^{-4} M for dye **3**. The feed ratio of HEMA/MeTMOS was 1/2. For the measurement of photoluminescence spectrum, the hybrid was excited at 387 nm.

spectra of the obtained white light-emitting hybrid with microwave irradiation. These dyes exhibited sharp emission peaks, and small overlaps between the emission of dye 1 and the absorption of dye 2, and between the emission of dye 2 and the absorption of dye 3 were observed, suggesting that the dyes doped into the hybrids can emit individual light without significant energy transfer between these dyes. The absolute luminescence quantum yield of the white light-emitting hybrid was 0.47. This high quantum yield might be accomplished because of less contribution from the quenching effects between the dyes.

Conclusions

We have investigated the energy transfer between organoboron dyes incorporated into the PHEMA-silica hybrids prepared by the microwave-assisted *in situ* method. The energy transfer between the dyes in the hybrids was suppressed as compared to the solution state due to the inhibition of dynamic quenching in the hybrid, in which the dyes are circumvented by silica matrices. Furthermore, we demonstrated the microwaveassisted preparation of white light-emitting hybrids by incorporating BGR dyes into the hybrids. The embedment and high

dispersion of the dyes in the hybrids allowed the bright and pure white light emission ($\Phi = 0.47$). The hybrids prepared by this method exhibit both sharp RGB light-emission peaks and pure white light emission, suggesting that they are applicable to the backlight for liquid crystal displays. Moreover, the emission color of the hybrids can be controlled by varying the amounts of organoboron dyes incorporated into the hybrids.

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