Selected Papers

Red/Near-Infrared Light-Emitting Organic–Inorganic Hybrids Doped with Covalently Bound Boron Dipyrromethene (BODIPY) Dyes via Microwave-Assisted One-Pot Process

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Red/near-infrared (NIR) light-emitting boron dipyrromethene (BODIPY) dyes bearing methacryloyl groups were synthesized, and these dyes were covalently bonded to poly(2-hydroxyethyl methacrylate) (PHEMA)–silica hybrids. The preparation of their hybrids was performed by simultaneous sol–gel reaction of trimethoxy(methyl)silane and radical copolymerization of 2-hydroxyethyl methacrylate (HEMA) with the dyes under microwave irradiation or conventional heating. Strong red/NIR light-emitting hybrids without discoloration of the dyes were successfully obtained under microwave irradiation, whereas the dyes lost luminescent properties in the hybrids prepared under conventional heating. Photostability test of the hybrids showed that covalent attachment of the dyes led to significant improvement in the photostability in comparison with the solution state. Further, elution amount of the dyes from the hybrids in organic solvents decreased relative to that from physical dye-admixing hybrids due to the covalent bond between PHEMA and the dyes.

Red/near-infrared (NIR) dyes have been widely used for application of light-emitting devices (LEDs),[1] optical communications,[2] dye lasers,[3] and bioimaging.[4] The advantages of imaging in the NIR region are absence or significant reduction of background absorption, fluorescence, and light scattering. Although red/NIR light-emitting dyes such as cyanines,[5] oxazines,[6] squaraines,[7] and carbopyronines[8] have been developed, these dyes suffer from poor photostability, aggregation, and low fluorescence quantum yields, especially in solid surroundings. Therefore, further improvements of red/NIR dyes are needed.

BODIPYs (4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacenes) and their derivatives are of particular interest because of high quantum yield, low rates of intersystem crossing, large molar absorption coefficients, and high photostability.[9] Recently, some red/NIR light-emitting BODIPY dyes and their derivatives have been reported. The modification of BODIPY dyes to red/NIR region has been conducted by attaching strongly electron-donating groups,[10] by rigidifying the structure,[11] by extending the conjugation of the system,[12] and by alternating the chromophore itself, such as an aza-BODIPY core.[13] Strong red/NIR light-emission of dyes in the solid state is necessary to fabricate high-performance red/NIR organic light-emitting devices (OLEDs). Generally, BODIPY dyes suffer from decrease of their luminescence intensity in the solid state due to the strong π–π stacking between the high planar structures of BODIPY molecules, which lead to serious self-quenching at high concentration.[14] In this regard, much effort has been devoted to avoid any decrease in luminescent efficiency in the solid state; e.g., bulky and rigid side chains are introduced into the BODIPY core to strengthen steric hindrance,[14] or the BODIPY dyes are incorporated into polymer[15] or silica matrices[16] to suppress crystallization of the dyes, i.e., formation of amorphous state by compositing polymer–silica matrices and the dyes.

Recently, organic dye-doped organic–inorganic hybrid materials have attracted much attention because they can share the characteristics of both organic moiety (flexibility and formability) and inorganic matrices (thermal and mechanical stability).[17] Highly luminescent hybrids can be achieved by homogeneous dispersion of the organic dyes in the hybrids. Various kinds of organic dyes at different wavelengths have been employed, and optical applications of the hybrids have been developed in the fields of light-emitting diodes (LEDs),[18] photochromic materials,[19] optical sensors,[20] and solid-state dye-lasers.[21,22] For example, Costela, Sastre, et al. have developed BODIPY dye-doped polymer–silica hybrids for solid-state dye lasers which have considerable laser efficiency and photostability.[22] Recently, they also reported red/NIR light-emitting organic–inorganic hybrids doped with perylene-

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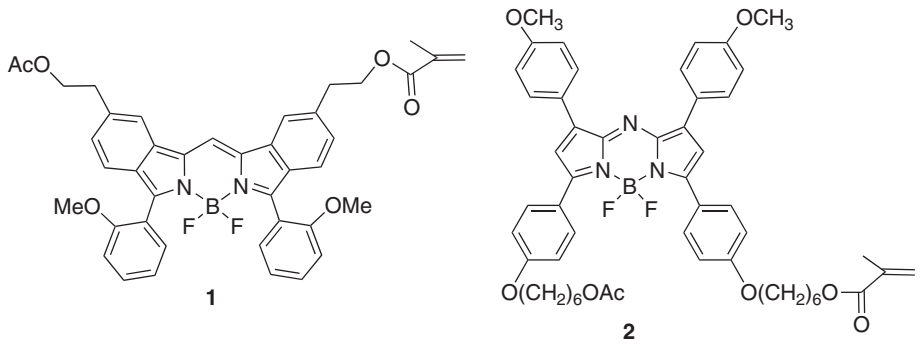


Scheme 1. Chemical structures of methacrylate-tethered red light-emitting dye **1** and NIR light-emitting dye **2**.

red,[3a] rhodamine,[3b] or hemicyanine dyes.[3b] However, there are no reports about red/NIR light-emitting BODIPY dye-doped organic–inorganic hybrids. In this paper, we demonstrate the preparation of red/NIR BODIPY dye-doped organic–inorganic hybrids. Recently, we reported microwave-assisted preparation of methacylate-tethered BODIPY-containing hybrids using an "in situ" method, i.e., the simultaneous sol–gel reaction of alkoxysilanes and radical copolymerization of vinyl compounds, in which microwave irradiation allowed the rapid synthesis of the hybrids and high dispersion of BODIPY dyes due to the accelerated reactions.[23] Moreover, it was found that covalent bonding between polymer and BODIPY dyes inhibits the elution of the dyes from the hybrids.[23] Based on these findings, we designed methacrylate-tethered red/NIR light-emitting BODIPY dyes which possess a boron di(iso)indomethene unit as a red light-emitting site, and a boron azadipyrromethene (aza-BODIPY) unit as an NIR light-emitting site, respectively (Scheme 1). Thus, we conducted simultaneous acetic acid-catalyzed sol–gel reaction of trimethoxy(methyl)silane (MeTMOS) and the radical copolymerization of 2-hydroxyethyl methacrylate (HEMA) with the obtained methacrylate-tethered BODIPY dyes under microwave irradiation, comparing to conventional heating as a heating method. Further, we investigated the optical properties (absorption and fluorescence), photostability, and leachability of the dyes obtained.

Experimental

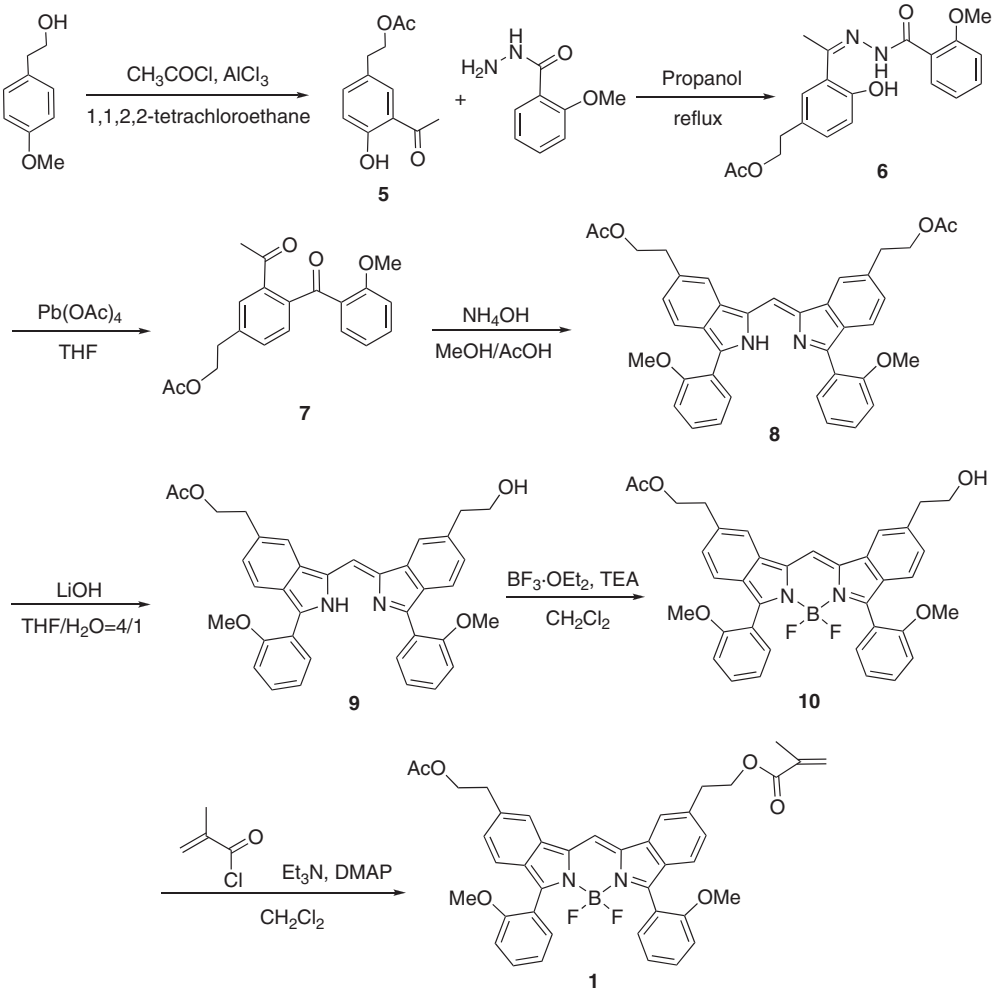
Materials. All reagents were obtained from commercial sources. 2-Hydroxyethyl methacrylate (HEMA) was distilled under reduced pressure. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol. Other reagents were used as received without further purification.

Synthesis of Methacrylate-Tethered Boron Di(iso)indomethene Dye. Methacrylate-tethered BODIPY dye **1** was synthesized according to Scheme 2.

Synthesis of 3-Acetyl-4-hydroxyphenethyl Acetate (5): Aluminium chloride (25.0 g, 0.188 mol) was added portionwise to a stirred solution of 4-methoxyphenethyl alcohol (8.11 g, 0.053 mol) and acetyl chloride (12.2 g, 0.155 mol) in 1,1,2,2-tetrachloroethane (80 mL), cooled in an ice-bath, at a rate sufficient to maintain the temperature between 0 and +5 °C. The mixture was stirred at room temperature for 22 h before pouring into crushed ice and separating the two phases. The aqueous phase was extracted with 1,1,2,2-tetrachloroethane (100 mL), and the combined organic extracts were washed with water, brine, dried over anhydrous magnesium sulfate, and then filtered and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (hexane/EtOAc = 9/1 → 7/3) to afford **5** (11.8 g, 89%) as a slightly yellowish oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 12.16 (s, 1H, Ar–O*H*), 7.56 (d, 1H, $J = 2.2$ Hz, Ar–*H*), 7.34 (dd, 1H, $J = 2.2$, 8.5 Hz, Ar–*H*), 6.93 (d, 1H, $J = 8.5$ Hz, Ar–*H*), 4.26 (t, 2H, $J = 6.9$ Hz, ArCH_2CH$_2$OAc), 2.90 (t, 2H, $J = 6.9$ Hz, –CH_2-OAc), 2.64 (s, 3H, Ar–(C=O)–CH_3), 2.05 (s, 3H, CH_3COO–). HRMS (APCI) Calcd for $C_{12}H_{15}O_4$ $[M + H]^+$: m/z 223.0970. Found: m/z 223.0971.

Synthesis of (*Z*)-4-Hydroxy-3-{1-[2-(2-methoxybenzoyl)-hydrazono]ethyl}phenethyl Acetate (6): A solution of 3-acetyl-4-hydroxyphenethyl acetate (**5**) (4.44 g, 20 mmol) and 2-methoxybenzohydrazide (4.99 g, 30 mmol) in 1-propanol (30 mL) was refluxed for 12 h. After cooling to room temperature, the resulting solid was collected by filtration, washed with 1-propanol, and then dried to give **6** (7.41 g, 91%). The obtained **6** was used for the next reaction without purification. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 13.02 (s, 1H, Ar–O*H*), 11.19 (s, 1H, >C=N–N*H*–(C=O)–), 7.83 (dd, 1H, $J = 1.7$, 7.7 Hz, Ar–*H*), 7.57 (m, 1H, Ar–*H*), 7.50 (d, 1H, $J = 2.0$ Hz, Ar–*H*), 7.23 (d, 1H, $J = 8.5$ Hz, Ar–*H*), 7.18 (dd, 1H, $J = 2.0$, 8.4 Hz, Ar–*H*), 7.12 (t, 1H, $J = 7.4$ Hz, Ar–*H*), 6.85 (d, 1H, $J = 8.3$ Hz, Ar–*H*), 4.19 (t, 2H, $J = 6.9$ Hz, ArCH_2CH$_2$OAc), 3.97 (s, 3H, –OCH_3), 2.85 (t, 2H, $J = 6.9$ Hz, –CH_2OAc), 2.42 (s, 3H, Ar–C(CH_3)=N–), 1.98 (s, 3H, CH_3COO–). HRMS (APCI) Calcd for $C_{20}H_{23}N_2O_5$ $[M + H]^+$: m/z 371.1607. Found: m/z 371.1596.

Synthesis of 3-Acetyl-4-(2-methoxybenzoyl)phenethyl Acetate (7): Lead tetraacetate (5.46 g, 16.8 mmol) was added to a solution of **6** (4.44 g, 12 mmol) in dry THF (100 mL) in small portions over a period of 5 min. After stirring at room temperature for 2 h, the resulting solid was removed by filtration. The filtrate was concentrated with a rotary evaporator and purified by silica gel column chromatography (hexane/EtOAc = 7/3 → 5/5) to give **7** (4.08 g, 92%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.59 (m, 1H, Ar–*H*), 7.51–7.42 (m, 2H, Ar–*H*), 7.34–7.27 (m, 2H, Ar–*H*), 7.06–6.94 (m, 2H, Ar–*H*), 4.32 (t, 2H, $J = 6.7$ Hz, ArCH_2CH$_2$OAc), 3.67 (s, 3H, Ar–OCH_3), 3.02 (t, 2H, $J = 6.7$ Hz, –CH_2OAc), 2.47 (s, 3H, Ar–(C=O)–CH_3), 2.04 (s, 3H, CH_3COO–). HRMS (APCI) Calcd for $C_{20}H_{21}O_5$ $[M + H]^+$: m/z 341.1389. Found: m/z 341.1377.

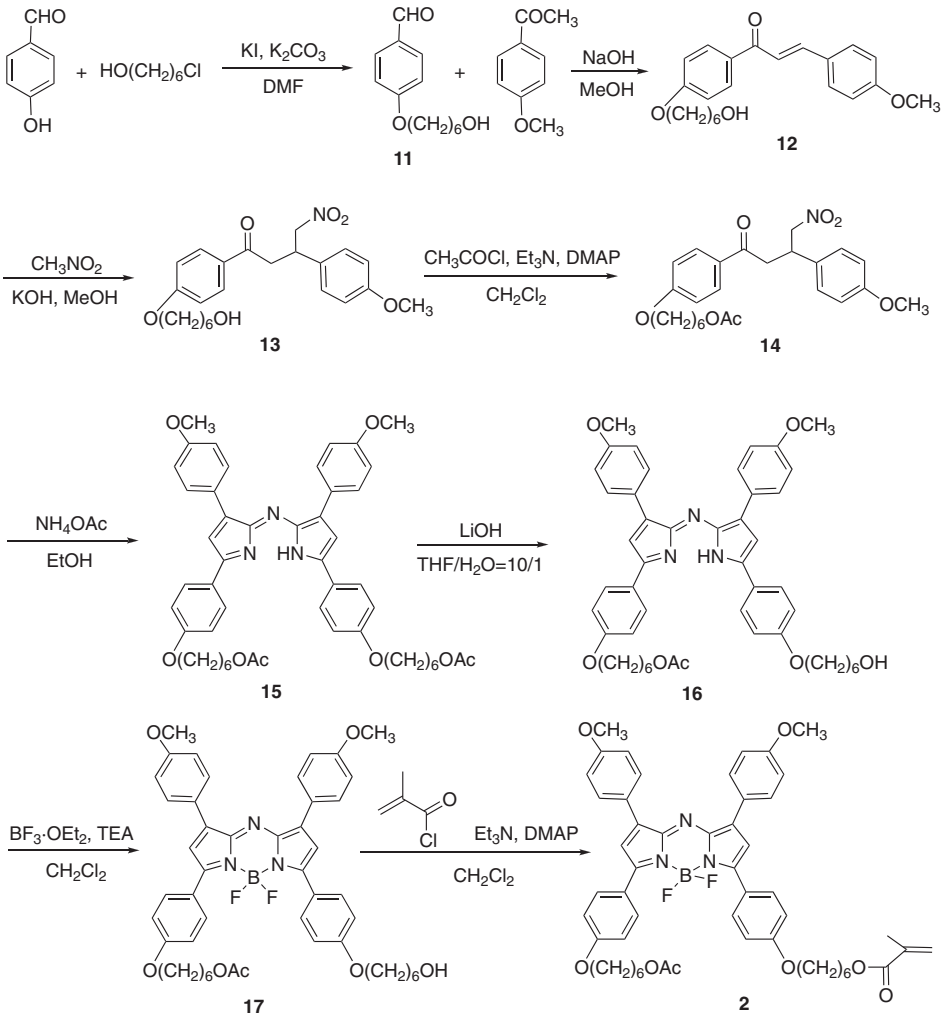


Scheme 2. Synthesis of methacrylate-tethered red light-emitting BODIPY dye **1**.

Synthesis of Diacetyl Di(iso)indomethene Ligand 8: Concentrated NH_4OH (NH_3 content 28–30%, 45 mL) was added to a solution of **7** (3.40 g, 10 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 and purified by silica gel column chromatography with $CHCl_3$ as an eluent to give **8** (1.49 g, 47%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.92 (d, 2H, $J = 6.7$ Hz, Ar–*H*), 7.78 (d, 4H, $J = 7.3$ Hz, Ar–*H*), 7.59 (s, 1H, Ar–C*H*=), 7.38 (t, 2H, $J = 7.9$ Hz, Ar–*H*), 7.10 (m, 4H, Ar–*H*), 7.04 (d, 2H, $J =$ 8.5 Hz, Ar–*H*), 4.42 (t, 4H, $J = 7.3$ Hz, ArCH_2CH_2OAc), 3.77 (s, 6H, Ar–OCH_3), 3.11 (t, 4H, $J = 7.3$ Hz, –CH_2OAc), 2.08 (s, 6H, CH_3COO–). HRMS (APCI) Calcd for $C_{39}H_{37}N_2O_6$ $[M + H]^+$: m/z 629.2652. Found: m/z 629.2639.

Synthesis of Monoacetyl Di(iso)indomethene Ligand 9: Lithium hydroxide monohydrate (0.252 g, 6.0 mmol) was added to a solution of **8** (1.26 g, 2.0 mmol) in 1.0 L of 4/1 (v/v) THF/distilled deionized H_2O under stirring. The solution was stirred at room temperature for 2 h. The reaction was quenched with 400 mL of saturated aqueous solution of NH_4Cl. THF was evaporated and the product was extracted with CH_2Cl_2 (300 mL × 3), dried with anhydrous magnesium sulfate and then the solution was filtered and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (hexane/EtOAc = 1/1 → 0/1) to afford **9** (1.18 g, 44%) as a metallic brown solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.92 (m, 2H, Ar–*H*), 7.78 (m, 4H, Ar–*H*), 7.59 (s, 1H, Ar–C*H*=), 7.38 (m, 2H, Ar–*H*), 7.10 (m, 4H, Ar–*H*), 7.04 (d, 2H, $J = 8.5$ Hz, Ar–*H*), 4.41 (t, 2H, $J = 7.3$ Hz, ArCH_2-CH_2OAc), 4.00 (t, 2H, $J = 6.5$ Hz, ArCH_2CH_2OH), 3.77 (s, 6H, Ar–OCH_3), 3.11 (t, 2H, $J = 7.3$ Hz, –CH_2OAc), 3.05 (t, 2H, $J = 6.5$ Hz, –CH_2OH), 2.08 (s, 3H, CH_3COO–). HRMS (APCI) Calcd for $C_{37}H_{35}N_2O_5$ $[M + H]^+$: m/z 587.2546. Found: m/z 587.2540.

Synthesis of Boron Di(iso)indomethene Dye 10: Dry triethylamine (0.98 mL, 7.0 mmol) was added to a solution of **9** (0.411 g, 0.70 mmol) in CH_2Cl_2 (250 mL), followed by addition of $BF_3 \cdot OEt_2$ (1.73 mL, 14 mmol). After the reaction mixture was stirred at 50 °C for 1 h, the solution was washed with water. The organic layer was separated, dried over anhydrous magnesium sulfate, and concentrated with a rotary evaporator to give a blue solid. The crude product was purified by silica gel column chromatography (hexane/EtOAc = 1/1) to afford **10** (0.320 g, 71%) as a metallic red-brown solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.80 (d, 1H, $J = 3.0$ Hz, Ar–*H*), 7.72 (m, 2H, Ar–*H*), 7.64 (d, 1H, $J = 6.8$ Hz, Ar–*H*), 7.52 (d, 1H, $J = 6.2$ Hz, Ar–C*H*=), 7.39 (m, 2H, Ar–*H*), 7.29 (m, 2H, Ar–*H*), 7.07–6.95 (m, 6H, Ar–*H*), 4.38 (t, 2H, $J = 7.0$ Hz,



Scheme 3. Synthesis of methacrylate-tethered NIR light-emitting BODIPY dye **2**.

ArCH_2CH$_2$OAc), 3.96 (t, 2H, $J = 5.9$ Hz, ArCH_2CH$_2$OH), 3.75 and 3.68 (s × 2, 6H, Ar–OCH_3), 3.08 (t, 2H, $J = 6.9$ Hz, –CH_2OAc), 3.02 (t, 2H, $J = 6.1$ Hz, –CH_2OH), 2.07 (s, 3H, CH_3COO–). HRMS (ESI) Calcd for $C_{37}H_{33}BF_2N_2O_5Na$ $[M + Na]^+$: m/z 657.2348. Found: m/z 657.2341.

Synthesis of Methacrylate-Tethered Boron Di(iso)indomethene Dye 1: Dry triethylamine (68 μL, 0.49 mmol) was added to a solution of **10** (0.258 g, 0.41 mmol) and 4-(dimethylamino)pyridine (5.0 mg, 41 μmol) in CH_2Cl_2 (10 mL), followed by addition of methacryloyl chloride (47 μL, 0.49 mmol) at room temperature. After stirring at room temperature for 12 h, the product was extracted with CH_2Cl_2 (200 mL) and water, and the organic layer was washed with water, saturated sodium hydrogencarbonate, brine, dried over anhydrous magnesium sulfate, and concentrated with a rotary evaporator to give a blue solid. The crude product was purified by silica gel column chromatography (hexane/EtOAc = 2/1) and recrystallization (THF/hexane) to afford **1** (0.199 g, 70%) as a metallic red-brown solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.80 (d, 1H, $J =$ 2.9 Hz, Ar–*H*), 7.73 (d, 2H, $J = 9.8$ Hz, Ar–*H*), 7.64 (d, 1H, $J = 7.6$ Hz, Ar–*H*), 7.53 (d, 1H, $J = 7.3$ Hz, Ar–C*H*=), 7.40 (m, 2H, Ar–*H*), 7.30 (d, 1H, $J = 3.2$ Hz, Ar–*H*), 7.28 (d, 1H, $J = 3.2$ Hz, Ar–*H*), 7.08–6.96 (m, 6H, Ar–*H*), 6.11 (s, 1H, CH_2=CCH$_3$–COO–), 5.57 (s, 1H, CH_2=CCH$_3$–COO–), 4.46 (t, 2H, $J = 7.1$ Hz, CH$_2$=CCH$_3$COOCH$_2$CH_2Ar), 4.39 (t, 2H, $J = 7.1$ Hz, ArCH_2CH$_2$OAc), 3.75 and 3.68 (s × 2, 6H, Ar–OCH_3), 3.14 (t, 2H, $J = 7.1$ Hz, CH$_2$=CCH$_3$COOCH_2CH$_2$Ar), 3.09 (t, 2H, $J = 7.1$ Hz, –CH_2OAc), 2.07 (s, 3H, CH_3COO–), 1.95 (s, 3H, CH$_2$=CCH_3COO–). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.1, 167.4, 157.7, 157.6, 138.9, 138.7, 136.3, 132.0, 130.9, 125.6, 123.8, 120.4, 120.2, 118.4, 114.7, 111.2, 111.0, 65.0, 64.7, 55.8, 55.6, 49.3, 35.7, 21.0, 18.3. ^{11}B NMR ($CDCl_3$, 128 MHz): δ 1.37 (t, $J = 37.6$, 25.0 Hz). HRMS (EI) Calcd for $C_{41}H_{37}BF_2N_2O_6$ $[M^+]$: m/z 702.2713. Found: m/z 702.2703. Anal. Calcd for $C_{41}H_{37}BF_2N_2O_6$: C, 70.09; H, 5.31; N, 3.99%. Found: C, 69.57; H, 5.53; N, 3.93%.

Synthesis of Methacrylate-Tethered Aza-BODIPY Dye. NIR light-emitting BODIPY dye **2** with a methacryloyl group was synthesized according to Scheme 3.

Synthesis of 4-(6-Hydroxyhexyloxy)benzaldehyde (11): Potassium iodide (0.830 g, 5.0 mmol) and potassium carbonate (13.8 g, 100 mmol) were added to a solution of 4-hydroxybenzaldehyde (6.11 g, 50 mmol) in dry *N*,*N*-dimethylformamide (100 mL) under nitrogen atmosphere. The mixture was heated at 90 °C, and then 6-chloro-1-hexanol (6.63 mL, 50 mmol) was added dropwise to the resulting solution, and further was

heated at 90 °C for 15 h. The mixture was poured into water (400 mL) and was extracted with three portions of 200 mL of a mixture of EtOAc/hexane (1/1). The combined organic layer was washed three times with 10% aqueous solution of sodium hydroxide (200 mL), twice with brine (200 mL), and dried over magnesium sulfate. The solvent was removed to yield the crude product by rotary evaporation. The obtained light yellow solid was ground and washed with hexane (60 mL) for 30 min, then filtered and dried under. Yield = 83%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.88 (s, 1H, –(C=O)–*H*), 7.83 (d, 2H, $J = 8.7$ Hz, Ar–*H*), 6.99 (d, 2H, $J = 8.5$ Hz, Ar–*H*), 4.05 (t, 2H, $J = 6.4$ Hz, Ar–OCH_2–), 3.67 (t, 2H, $J = 6.0$ Hz, –CH_2OH), 1.83 (m, 2H, Ar–OCH$_2$CH_2–), 1.66–1.37 (m, 7H, –CH_2CH_2CH_2-CH$_2$–O*H*). HRMS (APCI) Calcd for $C_{13}H_{19}O_3$ $[M + H]^+$: m/z 223.1334. Found: m/z 223.1324.

Synthesis of (*E*)-1-[4-(6-Hydroxyhexyloxy)phenyl]-3-(4-methoxyphenyl)-2-propenone (12): A solution of 4-(6-hydroxyhexyloxy)benzaldehyde (**11**) (8.89 g, 40 mmol) and 4′-methoxyacetophenone (6.01 g, 40 mmol) in absolute methanol (40 mL) was prepared under nitrogen at room temperature. Solid sodium hydroxide (0.160 g, 4.0 mmol) was added under nitrogen flow and the mixture was refluxed for 5 h. After the reaction was completed, the precipitate was filtered, washed with ethanol and water, and dried under vaccum to afford a slightly yellowish solid **12** (10.5 g, 74%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.03 (dt, 2H, $J = 8.8$, 2.5 Hz, Ar–*H*), 7.78 (d, 1H, $J = 15.5$ Hz, Ar–C*H*=CH–(C=O)–), 7.59 (dt, 2H, $J = 8.9$, 2.3 Hz, Ar–*H*), 7.43 (d, 1H, $J = 15.6$ Hz, Ar–CH=C*H*–(C=O)–), 6.98 (dt, 2H, $J = 8.8$, 2.5 Hz, Ar–*H*), 6.92 (dt, 2H, $J = 8.8$, 2.5 Hz, Ar–*H*), 4.01 (t, 2H, $J = 6.4$ Hz, Ar–OCH_2–), 3.89 (s, 3H, Ar–OCH_3), 3.67 (m, 2H, –CH_2OH), 1.83 (m, 2H, Ar–OCH$_2$CH_2–), 1.62 (m, 2H, –CH_2CH$_2$–OH), 1.56–1.41 (m, 4H, –CH_2CH_2CH$_2$CH$_2$–OH), 1.30 (t, 1H, $J = 5.4$ Hz, –CH$_2$–O*H*). HRMS (APCI) Calcd for $C_{22}H_{27}O_4$ $[M + H]^+$: m/z 355.1909. Found: m/z 355.1899.

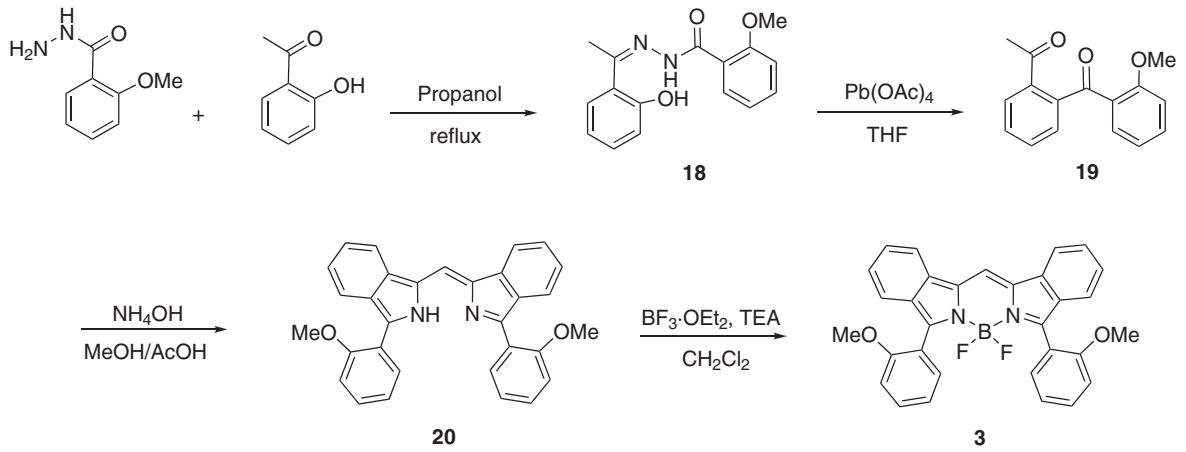
Synthesis of 1-[4-(6-Hydroxyhexyloxy)phenyl]-3-(4-methoxyphenyl)-4-nitrobutan-1-one (13): To a solution of **12** (3.94 g, 11.1 mmol) and potassium hydroxide (0.500 g, 8.9 mmol) in methanol (300 mL) was added nitromethane (11.9 mL, 222 mmol). The mixture was then heated under reflux for 24 h. The solution was cooled and the solvent was evaporated under vacuum. The product was extracted with EtOAc/water, and then the organic layer was washed with water, dried over anhydrous magnesium sulfate, and evaporated in vacuo. The residue product was purified by silica gel column chromatography (hexane/EtOAc = 1/2) to give **13** (3.80 g, 82%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.89 (dt, 2H, $J = 9.1$, 2.5 Hz, Ar–*H*), 7.17 (dt, 2H, $J = 8.6$, 2.6 Hz, Ar–*H*), 6.92 (dt, 2H, $J = 9.1$, 2.5 Hz, Ar–*H*), 6.83 (dt, 2H, $J = 8.6$, 2.6 Hz, Ar–*H*), 4.82–4.60 (m, 2H, –CH_2–NO$_2$), 4.14 (m, 1H, >C*H*CH$_2$–NO$_2$), 3.91 (t, 2H, $J = 6.5$ Hz, Ar–OCH_2–), 3.86 (s, 3H, Ar–OCH_3), 3.65 (t, 2H, $J = 6.6$ Hz, –CH_2OH), 3.35 (m, 2H, Ar–(C=O)–CH_2–), 1.77 (m, 2H, Ar–OCH$_2$CH_2–), 1.59 (m, 2H, –CH_2CH$_2$OH), 1.51–1.38 (m, 5H, –CH_2CH_2CH$_2$CH$_2$O*H*). HRMS (APCI) Calcd for $C_{23}H_{30}NO_6$ $[M + H]^+$: m/z 416.2073. Found: m/z 416.2063.

Synthesis of 6-{4-[3-(4-Methoxyphenyl)-4-nitrobutanoyl]-phenoxy}hexyl Acetate (14): Dry triethylamine (1.88 mL, 14 mmol) was added to a solution of **13** (3.74 g, 9.0 mmol) and 4-(dimethylamino)pyridine (55 mg, 0.45 mmol) in CH_2Cl_2 (20 mL), followed by addition of acetyl chloride (0.96 mL, 14 mmol) dissolved in CH_2Cl_2 (2.0 mL) at 0 °C. After stirring at room temperature for 18 h, the product was extracted with CH_2Cl_2 (200 mL), and the organic layer was washed with water, saturated sodium hydrogen carbonate, brine, dried over anhydrous magnesium sulfate, and concentrated with a rotary evaporator. The residue was purified by silica gel column chromatography (hexane/EtOAc = 3/1 → 2/1) to afford **14** (3.46 g, 84%) as a yellowish oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.92 (m, 2H, Ar–*H*), 7.30–7.17 (m, 2H, Ar–*H*), 6.93–6.82 (m, 4H, Ar–*H*), 4.80–4.62 (m, 2H, –CH_2–NO$_2$), 4.13 (m, 1H, >C*H*CH$_2$–NO$_2$), 4.07 (t, 2H, $J = 6.6$ Hz, –CH_2OAc), 3.91 (t, 2H, $J = 6.5$ Hz, Ar–OCH_2–), 3.87 (s, 3H, Ar–OCH_3), 3.36 (m, 2H, Ar–(C=O)–CH_2–), 2.04 (s, 3H, CH_3COO–), 1.77 (m, 2H, Ar–OCH$_2$CH_2–), 1.65 (m, 2H, –CH_2CH$_2$OAc), 1.53–1.36 (m, 4H, –CH_2CH_2CH$_2$CH$_2$OAc). HRMS (APCI) Calcd for $C_{25}H_{32}NO_7$ $[M + H]^+$: m/z 458.2179. Found: m/z 458.2170.

Synthesis of Diacetyl Azadipyrromethene Ligand 15: Ammonium acetate (42.1 g, 0.55 mol) was added to a solution of **14** (3.20 g, 7.0 mmol) in ethanol (100 mL). The mixture was refluxed for 24 h. The reaction solution was cooled to room temperature, and the solvent was concentrated to 50 mL, and filtered. The isolated solid was washed with a large amount of ethanol for several times. The residue was dried under vacuum to afford **15** (1.42 g, 49%) as a brown solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.03 (m, 4H, Ar–*H*), 7.88 (m, 4H, Ar–*H*), 7.05–6.94 (m, 10H, Ar–*H*), 4.09–4.04 (m, 8H, –CH_2OAc, Ar–OCH_2–), 3.90 (s, 6H, Ar–OCH_3), 2.04 (s, 6H, CH_3COO–), 1.85 (m, 4H, Ar–OCH$_2$CH_2–), 1.70 (m, 4H, –CH_2CH$_2$OAc), 1.55–1.48 (m, 8H, –CH_2CH_2CH$_2$CH$_2$OAc). HRMS (APCI) Calcd for $C_{50}H_{56}N_3O_8$ $[M + H]^+$: m/z 826.4067. Found: m/z 826.4061.

Synthesis of Monoacetyl Azadipyrromethene Ligand 16: Lithium hydroxide monohydrate (0.315 g, 7.5 mmol) was added to a solution of **15** (1.24 g, 1.5 mmol) in 10/1 (v/v) THF/distilled deionized water (330 mL) under stirring. The solution was stirred at room temperature for 1.5 h. The reaction was quenched with 50 mL of saturated aqueous solution of NH_4Cl. THF was evaporated and the product was extracted with CH_2Cl_2 (150 mL × 6), dried with anhydrous magnesium sulfate, and then the solution was filtered and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (hexane/EtOAc = 9/1 → 7/3 → 5/5) to afford **16** (0.178 g, 15%) as a metallic brown solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.02 (m, 4H, Ar–*H*), 7.88 (m, 4H, Ar–*H*), 7.04 (m, 6H, Ar–*H*), 6.95 (m, 4H, Ar–*H*), 4.09–4.04 (m, 6H, –CH_2OAc, Ar–OCH_2–), 3.91 (s, 6H, Ar–OCH_3), 3.65 (t, 2H, $J = 6.7$ Hz, –CH_2OH), 2.06 (s, 3H, CH_3COO–), 1.85 (m, 4H, Ar–OCH$_2$CH_2–), 1.71–1.46 (m, 12H, Ar–OCH$_2$CH$_2$CH_2CH_2-CH_2CH$_2$–). HRMS (ESI) Calcd for $C_{48}H_{54}N_3O_7$ $[M + H]^+$: m/z 784.3962. Found: m/z 784.3949.

Synthesis of Aza-BODIPY Dye 17: Dry triethylamine (0.59 mL, 4.2 mmol) was added to a solution of **16** (0.33 g, 0.42 mmol) in CH_2Cl_2 (150 mL), followed by addition of $BF_3 \cdot OEt_2$ (1.04 mL, 8.4 mmol). After the reaction mixture was stirred at 50 °C for 1 h, the solution was washed with water. The organic layer was separated, dried over anhydrous magnesium sulfate, and then concentrated by rotary evaporation. The residue was purified by silica gel column chromatography



Scheme 4. Synthesis of boron di(iso)indomethene dye **3**.

($CHCl_3$/acetone = 19/1) to afford **17** (0.060 g, 17%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.05 (m, 8H, Ar–*H*), 7.01–6.93 (m, 10H, Ar–*H*), 4.11–4.04 (m, 6H, –C*H*$_2$OAc, Ar–OC*H*$_2$–), 3.88 (s, 6H, Ar–OC*H*$_3$), 3.69 (m, 2H, –C*H*$_2$OH), 2.06 (s, 3H, C*H*$_3$COO–), 1.86 (m, 4H, Ar–OCH$_2$C*H*$_2$–), 1.76–1.45 (m, 12H, Ar–OCH$_2$-CH$_2$C*H*$_2$C*H*$_2$C*H*$_2$CH$_2$–). HRMS (APCI) Calcd for $C_{48}H_{53}BF_2N_3O_7$ $[M + H]^+$: *m*/*z* 832.3945. Found: *m*/*z* 832.3949.

Synthesis of Methacrylate-Tethered Aza-BODIPY Dye 2: Dry triethylamine (67 µL, 0.48 mmol) was added to a solution of **17** (0.204 g, 0.24 mmol) and 4-(dimethylamino)pyridine (3.0 mg, 0.024 mmol) in CH_2Cl_2 (30 mL), followed by addition of methacryloyl chloride (47 µL, 0.48 mmol) at room temperature. After stirring at room temperature for 4 h, the product was extracted with CH_2Cl_2 (200 mL) and water, and the organic layer was washed with water, saturated sodium hydrogen carbonate, brine, dried over anhydrous magnesium sulfate, and then concentrated with a rotary evaporator. The crude product was purified by silica gel column chromatography ($CHCl_3$/acetone = 19/1) to afford **2** (59 mg, 27%) as a deep green solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.05 (m, 8H, Ar–*H*), 7.01–6.93 (m, 10H, Ar–*H*), 6.11 (s, 1H, C*H*$_2$=CCH$_3$–COO–), 5.55 (s, 1H, C*H*$_2$=CCH$_3$–COO–), 4.18 (m, 2H, CH$_2$=CCH$_3$-COOC*H*$_2$–), 4.11–4.04 (m, 6H, –C*H*$_2$OAc, Ar–OC*H*$_2$–), 3.88 (s, 6H, Ar–OC*H*$_3$), 2.06 (s, 3H, C*H*$_3$COO–), 1.95 (s, 3H, CH$_2$=CC*H*$_3$COO–), 1.86 (m, 4H, Ar–OCH$_2$C*H*$_2$–), 1.72 (m, 4H, Ar–OCH$_2$CH$_2$CH$_2$CH$_2$C*H*$_2$CH$_2$–), 1.62–1.40 (m, 8H, Ar–OCH$_2$CH$_2$C*H*$_2$C*H*$_2$CH$_2$CH$_2$–). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.2, 167.5, 161.7, 160.2, 157.7, 145.1, 143.7, 136.5, 131.4, 130.7, 125.2, 124.4, 117.0, 114.6, 114.1, 67.9, 64.6, 64.4, 55.4, 29.1, 28.5, 25.8, 25.8, 21.0, 18.3. ^{11}B NMR ($CDCl_3$, 128 MHz): δ 0.68 (t, *J* = 37.6, 25.0 Hz). HRMS (FAB) Calcd for $C_{52}H_{56}BF_2N_3O_8$ $[M^+]$: *m*/*z* 899.4129. Found: *m*/*z* 899.4105. Anal. Calcd for $C_{52}H_{56}BF_2N_3O_8$: C, 69.41; H, 6.27; N, 4.67%. Found: C, 68.47; H, 6.65; N, 4.43%.

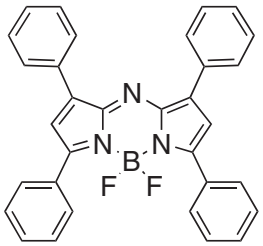
Synthesis of Boron Di(iso)indomethene Dye. Red light-emitting BODIPY dye **3** was synthesized as shown in Scheme 4.

Synthesis of (*Z*)-*N*′-[1-(2-Hydroxyphenyl)ethylidene]-2-methoxybenzohydrazide (18): A solution of *o*-hydroxyacetophenone (4.08 g, 30 mmol) and 2-methoxybenzohydrazide (7.48 g, 45 mmol) in 1-propanol (40 mL) was refluxed for 12 h. After cooling to room temperature, the resulting solid was collected by filtration, washed with 1-propanol, and dried to give **18** (8.53 g, 97%). The obtained **18** was used for the next reaction without purification. ^{1}H NMR ($CDCl_3$, 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–). HRMS (APCI) Calcd for $C_{16}H_{17}N_2O_3$ $[M + H]^+$: *m*/*z* 285.1239. Found: *m*/*z* 285.1240.

Synthesis of 1-[2-(2-Methoxybenzoyl)phenyl]ethanone (19): Lead tetraacetate (5.47 g, 16.8 mmol) was added to a solution of **18** (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 with a rotary evaporator and purified by silica gel column chromatography ($CHCl_3$) to give **19** (2.86 g, 94%). ^{1}H NMR ($CDCl_3$, 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, –OC*H*$_3$), 2.49 (s, 3H, Ar–(C=O)–C*H*$_3$). HRMS (APCI) Calcd for $C_{16}H_{15}O_3$ $[M + H]^+$: *m*/*z* 255.1021. Found: *m*/*z* 255.1021.

Synthesis of Di(iso)indomethene Ligand 20: Concentrated NH_4OH (NH_3 content 28–30%, 45 mL) was added to a solution of **19** (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 give a crude product. The crude product was purified by silica gel column chromatography with hexane/$CHCl_3$ = 1/1 as an eluent to give **20** (1.52 g, 62%). ^{1}H NMR ($CDCl_3$, 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–C*H*=), 7.35 (m, 4H, Ar–*H*), 7.24 (m, 2H, Ar–*H*), 7.11 (t, 2H, *J* = 7.2 Hz, Ar–*H*), 7.04 (d, 2H, *J* = 8.5 Hz, Ar–*H*), 3.76 (s, 6H, –OC*H*$_3$). HRMS (APCI) Calcd for $C_{31}H_{25}N_2O_2$ $[M + H]^+$: *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 **20** (0.562 g, 1.23 mmol) in CH_2Cl_2 (500 mL), followed by addition of $BF_3 \cdot OEt_2$ (3.04 mL, 24.6 mmol). After the reaction mixture was stirred at 50 °C for 16 h, the solution was washed with water. The organic layer was separated, dried over



4

Scheme 5. Chemical structure of aza-BODIPY dye **4**.

anhydrous magnesium sulfate, and concentrated by a rotary evaporator to give a blue solid. The crude product was purified by silica gel column chromatography ($CHCl_3$) to afford **3** (0.50 g, 81%) as a metallic red-brown solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 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–C*H*=), 7.44–7.39 (m, 4H, Ar–*H*), 7.36–7.33 (m, 2H, Ar–*H*), 7.17 (m, 2H, Ar–*H*), 7.08–6.96 (m, 4H, Ar–*H*), 3.76 and 3.68 (s × 2, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 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. ^{11}B NMR ($CDCl_3$, 128 MHz): δ 1.47 (t, $J = 37.6$, 25.0 Hz). 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 Aza-BODIPY Dye. Aza-BODIPY **4** without a methacryloyl group was prepared according to the literature (Scheme 5).[13]

Preparation of BODIPY-Containing Polymer–Silica Hybrid Luminescent Materials.[23] 2-Hydroxyethyl methacrylate (HEMA; 1.00 g, 7.70×10^{-3} mol), and 2,2′-azobis(isobutyronitrile) (AIBN; 2.52 mg) were dissolved in methanol, followed by adding trimethoxy(methyl)silane (MeTMOS; 2.00 g) and 0.10 M aqueous acetic acid solution (1.00 mL). The solution was stirred under ambient atmosphere for 3 h to promote hydrolysis of MeTMOS, and then 1.54–7.70×10^{-7} mol of **1** (0.154–0.770 mL of THF solution (1.0×10^{-3} M)) or 1.54–7.70×10^{-7} mol of **2** (dissolved in 3 mL of THF) were added. The molar ratios of HEMA/dyes were 10000/1–50000/1 for each dye. The concentrations of the dyes in the solution were 2.2×10^{-5}–1.1×10^{-4} M. A half of the solution was poured into a polypropylene vessel ($\phi = 33$ mm, $h = 36$ mm), and put into a microwave reactor (Milestone General MicroSYNTH). 2.45 GHz microwave was irradiated under nitrogen atmosphere for the prescribed conditions. For the conventional heating, the other half of the solution was put into a 60 °C oven under argon atmosphere for 24 h.

Evaluation of Photostability of Hybrids. The photostability of the hybrids was investigated by following absorbance (A) of the hybrids under continuous UV irradiation (365 nm). The ratio of A to initial absorbance of the hybrids (A_0) was plotted as a function of the irradiation time. The distance between the UV lamp and the samples of the hybrids was 1 cm. A transilluminator (UVP, LMS-20E, 6500 μW cm^{-2} at 365 nm) was used as an UV source. Absorbances of the samples of the hybrids were corrected for the value at 720 nm.

Elution Test of Hybrids. The elution test of the hybrids was carried out as follows. 0.25 g of the hybrid was immersed in 5.0 mL of acetone. After 48 h, absorbance of the eluted dye solution was measured by UV–vis spectroscopy. From the calibration curve of the absorbance of dye, the concentration of the dye in acetone solution was determined. The elution percentages of dyes were calculated from the ratio of the concentration of the eluted dye solution and ideal dye concentration when all dyes were eluted from the hybrid.

Measurements. ^{1}H (400 MHz), ^{13}C (100 MHz), and ^{11}B (128 MHz) NMR spectra were recorded on a JEOL JNM-EX400 spectrometer. ^{1}H and ^{13}C NMR spectra used tetramethylsilane (TMS) as an internal standard, and ^{11}B NMR spectra were referenced externally to $BF_3 \cdot OEt_2$ (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. Absolute luminescent quantum yields were obtained by integrating sphere. A sample of the hybrids was set in the integrating sphere, and the spectra were recorded with the fluorescence spectrometer. The quantum yields were determined by the calculator software.

Results and Discussion

Synthesis of Red/NIR Light-Emitting BODIPY Dyes. We designed and prepared red light-emitting dye **1** and NIR light-emitting dye **2** based on boron di(iso)indomethene and aza-BODIPY skeletons, respectively (Scheme 1). A methacryloyl group was introduced into respective BODIPY dyes **1** and **2** to form covalent bonds between the dyes and HEMA, probably leading to suppression of the elution of the dyes from the PHEMA–silica hybrids.[23]

Preparation of BODIPY dye **1** tethered with a methacryloyloxy group is outlined in Scheme 2. 3-Acetyl-4-hydroxyphenethyl acetate (**5**), which was prepared by Fries rearrangement of 4-methoxyphenethyl alcohol with acetyl chloride in the presence of $AlCl_3$, was reacted with 2-methoxybenzohydrazide, and then oxidized with $Pb(OAc)_4$ to give the substituted 2-acylacetophenone **7**. Next, the diethyl acetate-substituted di(iso)indomethene ligand **8** was prepared via condensation of **7** with ammonia. It was hydrolyzed with lithium hydroxide monohydrate to give the monoalcohol di(iso)indomethene ligand **9**, and then treated with boron trifluoride to give the boron di(iso)indomethene-based compound **10**. Further reaction of methacryloyl chloride with **10** afforded methacryloyl-substituted BODIPY dye **1** exhibiting red emission.

BODIPY dye **2** having an aza-BODIPY moiety and a methacryloyl group was prepared as shown in Scheme 3. For the improvement of solubility of the aza-BODIPY dye, long alkyl chains were introduced into the aza-BODIPY skeleton. First, diaryl α,β-unsaturated ketone **12** was prepared by an aldol/dehydration reaction of the corresponding 4-(6-hydroxyhexyloxy)benzaldehyde (**11**) and 4-methoxyacetophenone. Next, Michael addition of nitromethane to the α,β-unsaturated ketone gave the 1,3-diaryl-4-nitrobutanone **13**. After acetylation of **13**, the obtained compound **14** was condensed with ammonium acetate in ethanol to afford the diacetyl azadipyrromethene **15**. Hydrolysis of **15** with lithium hydroxide monohydrate was carried out to obtain the monoacetyl

Table 1. Spectroscopic Data of BODIPY Dyes[a)]

Dye	λ_{max}(abs) /nm	ε_{max}	λ_{max}(em) /nm	Φ_F
1	625	109100	649	0.53
2	694	83600	714	0.080

a) Measured in THF (1.0×10^{-6} M).

compound **16**, and then $BF_3 \cdot OEt_2$ was treated to give the aza-BODIPY compound **17**. Finally, methacryloyl chloride was reacted with the aza-BODIPY to yield the methacrylate-tethered aza-BODIPY dye **2**.

The photophysical properties of **1** and **2** in THF solution are summarized in Table 1. The absorptions of **1** and **2** are characterized by strong $S_0 \rightarrow S_1$ ($\pi \rightarrow \pi^*$) transition at around 625 and 694 nm, respectively, and these dyes exhibited a large molar absorption coefficient ($\varepsilon_{max} > 10^4$). Upon excitation at 625 nm, the dye **1** emits deep red light at 649 nm, and shows relatively high quantum yield. In contrast, emission maximum of dye **2** was at 714 nm in the NIR region (excited at 694 nm), while dye **2** possesses lower quantum yield. This low quantum yield is due to increased internal conversion according to the energy gap law stating that the nonradiative deactivation probability of $S_1 \rightarrow S_0$ increases as the energy gap of $S_0 \rightarrow S_1$ decreases.[24]

Preparation and Photophysical Properties of Red/NIR Dye-Containing Organic–Inorganic Hybrids. Organic–inorganic hybrids containing the obtained dyes **1** and **2** were prepared by the "in situ" method, which is the simultaneous reaction of radical copolymerization of organic monomers and the sol–gel reaction of silica precursors.[3,22,23] 2-Hydroxyethyl methacrylate (HEMA) was used as a polymerizable comonomer of the methacrylate-tethering BODIPY dyes **1** and **2**, and trimethoxy(methyl)silane (MeTMOS) as an alkoxysilane for the formation of silica matrices. The molar ratios of HEMA/BODIPY dyes were 10000/1–50000/1, and the feed ratio of HEMA/MeTMOS was 1/2. Here, AIBN and acetic acid were employed as a radical initiator and a catalyst of sol–gel reaction of MeTMOS, respectively. These reactions were carried out under microwave irradiation and conventional heating. Microwave irradiation conditions in the preparation were 30 W for 40 min, 100 W for 10 min, and 300 W for 5 min, sequentially. Under conventional heating, the hybrids were prepared in an oven at 60 °C for 24 h.

The appearances of the hybrids prepared under both heating methods are shown in Figure 1. In the case that dye **1** was employed, a transparent blue hybrid with strong red light emission was obtained under microwave irradiation (Figures 1a and 1c). On the other hand, the hybrid prepared under conventional heating was pale green and emitted slightly blue light (Figures 1b and 1d). UV–vis spectra of these hybrids are illustrated in Figure 2. A maximum absorption peak wavelength of the hybrid prepared under microwave irradiation was 625 nm, which is the same absorption wavelength of dye **1** in THF solution. In the hybrid prepared under conventional heating, the absorption peak of dye **1** decreased drastically, and another absorption peak appeared at 420 nm, probably corresponding to decomposition of dye, so that the conventional

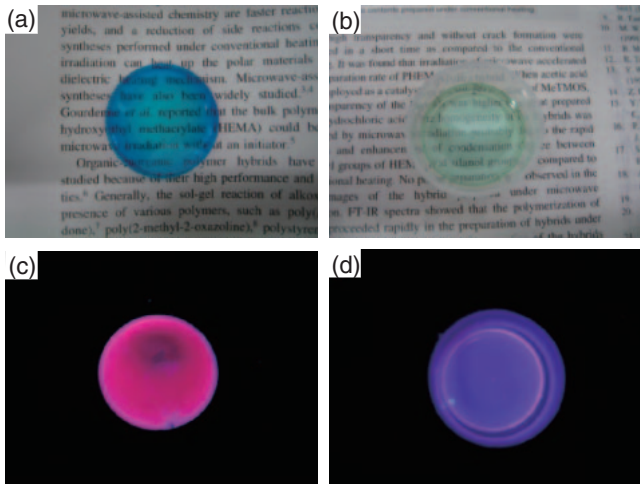


Figure 1. Photographs of BODIPY dye **1**-containing PHEMA–silica hybrids prepared under (a, c) microwave irradiation and (b, d) conventional heating, (a, b) appearance, (c, d) under UV irradiation. The molar ratio of HEMA/**1** was 20000/1.

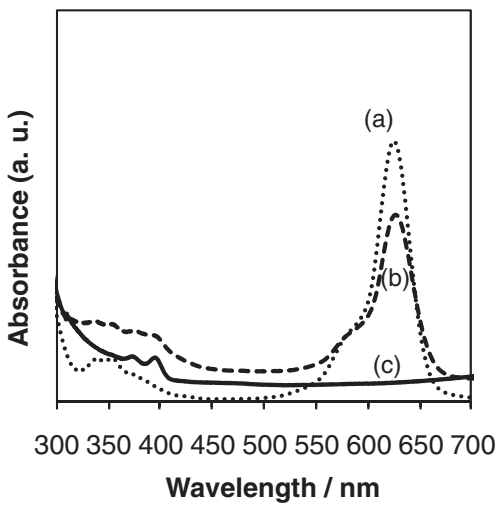


Figure 2. Absorption spectra of (a) BODIPY dye **1** (1.0×10^{-5} M THF solution), and dye **1**-containing PHEMA–silica hybrids prepared under (b) microwave irradiation and (c) conventional heating. The feed ratio of HEMA/MeTMOS was 1/2. The molar ratio of HEMA/**1** was 10000/1.

heating method might lead to the discoloration of the dye in the hybrid. In the case of dye **2**, transparent grayish hybrids were obtained under microwave irradiation, while colorless hybrids were obtained under conventional heating (Figure 3). As shown in Figure 4, the NIR absorption band of dye **2** at 694 nm was retained in the hybrids prepared under microwave irradiation. However, a small absorption band was observed in the hybrids prepared under conventional heating. The changes of the absorption bands observed in the hybrids prepared under conventional heating are probably because these dyes are exposed to heating for a long period in the presence of acid. The hybrids can be prepared in a short time (55 min) under microwave irradiation. Consequently, microwave irradiation

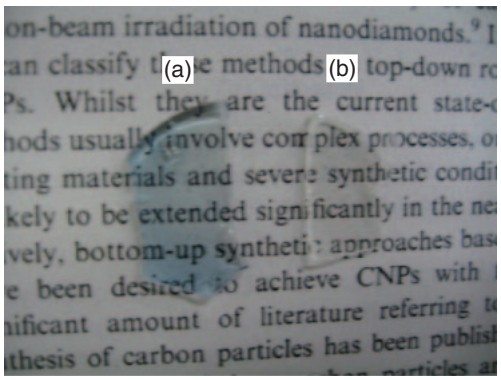


Figure 3. Appearances of BODIPY dye **2**-containing PHEMA/silica hybrids prepared under (a) microwave irradiation and (b) conventional heating. The molar ratio of HEMA/**2** was 20000/1.

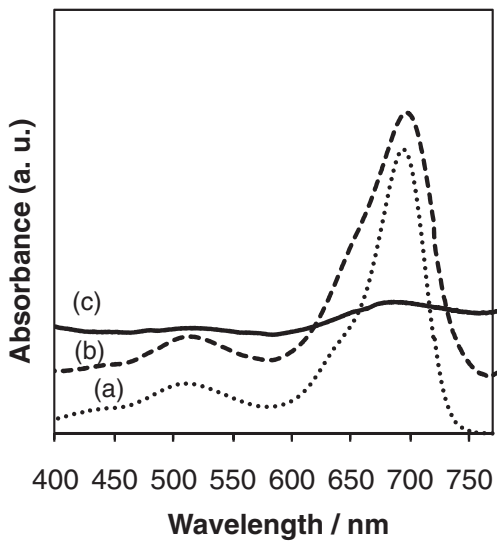


Figure 4. Absorption spectra of (a) BODIPY dye **2** (1.0×10^{-5} M THF solution), and dye **2**-containing PHEMA–silica hybrids prepared under (b) microwave irradiation and (c) conventional heating. The feed ratio of HEMA/MeTMOS was 1/2. The molar ratio of HEMA/**2** was 10000/1.

allows the rapid preparation of BODIPY dye-doped hybrids before the decomposition/discoloration of the dyes. This is probably due to two reasons: The conversion of HEMA monomer under microwave irradiation was higher than that under conventional heating in the preparation of PHEMA–silica using an in situ method,[25] and the sol–gel reaction of tetramethoxysilane (TMOS) is accelerated by microwave irradiation.[26] Therefore, it can be concluded that the microwave irradiation enhances both the polymerization rate of HEMA and the sol–gel reaction of MeTMOS.

Photoluminescence properties of the dyes **1** and **2** in THF solution and the BODIPY dye-containing hybrids prepared under both methods are shown in Figures 5 and 6, respectively. When the molar ratio of HEMA/**1** was 10000/1, the emission maximum of the dye **1**-doped hybrid prepared under microwave irradiation was 647 nm, which is similar to that in THF solution (1.0×10^{-6} M), indicating that the dye **1** was

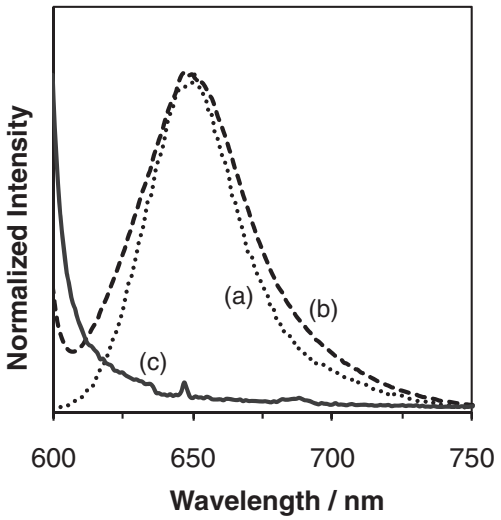


Figure 5. Photoluminescence spectra of (a) BODIPY dye **1** (1.0×10^{-6} M THF solution), and dye **1**-containing PHEMA–silica hybrids prepared under (b) microwave irradiation and (c) conventional heating. The feed ratio of HEMA/MeTMOS was 1/2. The molar ratio of HEMA/**1** was 10000/1. Excitation wavelength: 590 nm.

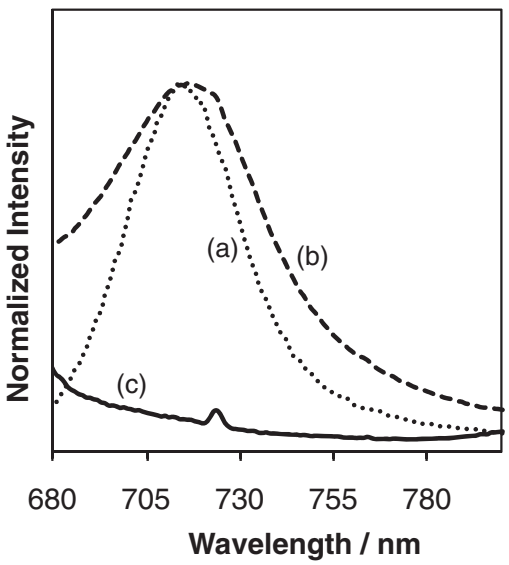


Figure 6. Photoluminescence spectra of (a) BODIPY dye **2** (1.0×10^{-6} M THF solution), and dye **2**-containing PHEMA–silica hybrids prepared under (b) microwave irradiation and (c) conventional heating. The feed ratio of HEMA/MeTMOS was 1/2. The molar ratio of HEMA/**2** was 10000/1. Excitation wavelength: 660 nm.

dispersed homogeneously. The hybrid prepared under conventional heating emitted weak red light, and the maximum at 647 nm almost disappeared. In the case of the dye **2**, the hybrid prepared under microwave irradiation showed the emission maximum at 716 nm, which is almost identical to that of dye **2** in THF solution (1.0×10^{-6} M). On the other hand, the photoluminescence of the hybrid prepared under conventional heating was quite small.

Quantum yields of the hybrids prepared under microwave irradiation and the dyes in the solution and solid states are

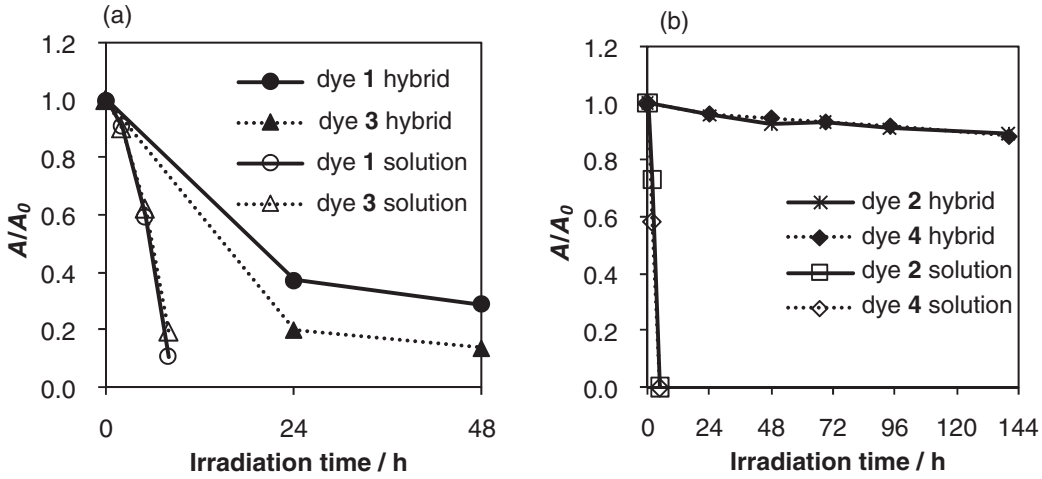


Figure 7. Photostability of solution and dye-incorporated PHEMA–silica hybrids prepared under microwave irradiation. (a) Red light-emitting dye **1** and **3**. (b) NIR light-emitting dye **2** and **4**. Concentrations of dye solutions were 1.0×10^{-5} M. In the preparation of hybrids, the feed ratio of HEMA/MeTMOS was 1/2, and the molar ratio of HEMA/dye was 10000/1.

Table 2. Quantum Yields of BODIPY-Containing PHEMA–Silica Hybrids[a)] under Microwave Irradiation and the Dyes in the Solution and the Solid States

Dye	Hybrid microwave (HEMA/dye)			Solution (THF)[b)]	Solid state
	10000/1	20000/1	50000/1		
1	0.41	0.49	0.53	0.53	0
2	0.032	0.084	0.12	0.080	0

a) HEMA (1.00 g), **1** or **2**, and AIBN (2.52 mg) were dissolved in methanol (3.0 mL), followed by adding MeTMOS (2.00 g) and 0.10 M acetic acid aqueous solution (1.0 mL). Microwave irradiation was carried out with three steps; 30 W for 40 min, 100 W for 10 min, and 300 W for 5 min. b) 1.0×10^{-6} M.

listed in Table 2. The hybrids prepared under microwave irradiation exhibited sufficiently high quantum yield as well as the dyes **1** and **2** in THF solution when the molar ratio of HEMA/dye was 50000/1. In sharp contrast, these dyes in solid state exhibited no photoluminescence due to strong π–π stacking between the planar structures of BODIPY molecules.[14] Accordingly, the incorporation of the dyes into the hybrids inhibited the inter- and intramolecular π–π stacking between each dye in the polymer side chain, leading to the highly intense photoluminescence in the solid state.

Evaluation of Photostability and Leachability of BODIPY Dyes Incorporated into the Hybrids: The Effect of Covalent Bonding between PHEMA and Dyes. The photostability of the BODIPY-containing hybrids, in which the molar ratio of HEMA/dyes was 10000/1, was evaluated by continuous UV irradiation (365 nm). Figure 7 shows the plots of the ratio of the absorbance after certain UV irradiation time to initial absorbance (A/A_0). The dyes **3** and **4** without methacryloyl groups were used as a comparison of the dyes **1** and **2**, respectively. The photostability of all dyes was increased by incorporation into the hybrids compared to the solution state probably because of limitation of the access of oxygen in the excited state of the dyes. Although the absorbance of red light-emitting dye-containing hybrids decreased gradually under UV irradiation, the decrease of dye **1** was slower than that of dye **3**, indicating that the covalent bonds between PHEMA and the dyes play an important role in the photostability of the dyes. On the other hand, the dye **2**-containing hybrid showed high photostability as well as the dye **4**-containing hybrid. The photostability of the dyes incorporated into the hybrids was higher than that of the dyes in the solution. Photobleaching of dyes can be reduced in an inert atmosphere.[27] Accordingly, surrounding luminescent dye-containing polymer with silica matrices allows high photostability of the dyes possibly because of limitation of the access of oxygen in the excited state of the dye.

Elution amount of the dyes from the hybrids was investigated by immersing the hybrids into acetone. After 48 h, the elution amount of dye **1** was 0.67%, much smaller than that of dye **3** (14%), indicating that the elution amount of dye **1** from the hybrid is inhibited due to covalently attachment between the dye and HEMA polymer. Similarly, the elution amount of dye **2** from the hybrid was 19%, smaller than that of aza-BODIPY without methacryloyl group **4** (32%). The elution amount of dye **2** from the hybrids was larger than that of dye **1**, probably because unreacted dye **2** might exist in the hybrids.

Conclusion

We have demonstrated the preparation of red/NIR light-emitting organic–inorganic hybrids, where the copolymerization of BODIPY dyes **1** and **2** with HEMA was carried out simultaneously with the sol–gel reaction of MeTMOS. Incorporation of these BODIPY dyes into hybrids allowed strong luminescence in the solid state. Microwave irradiation led to rapid synthesis of red/NIR dye-doped hybrids with inhibited discoloration of the dyes. These dyes were dispersed homogeneously, and showed good optical properties. The photostability of these dyes was improved by incorporation into hybrids compared to the solution state. Further, the elution of BODIPY dyes from the hybrids prepared by the in situ method was significantly reduced compared with that from the hybrids with noncovalent bond between PHEMA and the dyes. The

obtained hybrids are expected to be applicable to various optical applications such as OLEDs, telecommunications, and sensors.

Supporting Information

^{1}H NMR, and HRMS of the dyes **1**, **2**, and **3**. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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