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Aromatic Ring-Fused BODIPY-Based Conjugated Polymers Exhibiting Narrow Near-Infrared Emission Bands

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ABSTRACT: Three conjugated copolymers, consisted of alternating *p*-phenylene-ethynylene and boron di(iso)indomethene units in the backbone, were synthesized via palladium-catalyzed Sonogashira coupling reaction of 1,4-diethynyl-2,5-dihexadecyloxybenzene and three diiodophenyl-fused BODIPY monomers. The structures and properties of the conjugated polymers were characterized by ^{1}H NMR, ^{11}B NMR, and Fourier transform infrared (FT-IR) spectroscopies, elemental analysis, size exclusion chromatography (SEC), UV−vis absorption spectroscopy, photoluminescence (PL) spectroscopy, and theoretical calculation using density-functional theory (DFT) method. The polymers obtained were fusible and soluble in common organic solvents including THF, benzene, toluene, $CHCl_3$, and CH_2Cl_2, etc. The incorporation of the indomethene monomers into *p*-phenylene-ethynylene main chain led to red shifts in UV-absorption and PL spectra by extended π-conjugation of the copolymers in comparison with the monomers. Accordingly, the copolymers emitted in the range from deep-red to near-infrared region with emission spectral maxima at around 691−720 nm and exhibited high quantum yields (Φ_F = 33−49%). The photostabilities of the polymers were examined by monitoring decrease of the PL spectra under continuous UV irradiation using a UV lamp under aerobic conditions. Further, their thermal stabilities were also investigated by TGA measurement.

Introduction

Organoboron dyes with light-emitting ability are of increasing interest for not only chemistry and material science but also biological science. Many organoboron dyes have been used as chemical probes,[1] photosensitizers,[2] and optical sensing[3] due to large molar extinction coefficients and two-photon absorption cross sections, high emission quantum yields (Φ_F), and sensitivity to the surrounding medium.[4] Recently, the incorporation of several organoboron dyes into a polymer main chain, side chain, and initial end is more attractive for application as electroluminescent devices, organic field-effect transistors, photovoltaics, etc. For example, Jäkle et al. have reported that novel well-defined organoboron quinolate polymers were synthesized by the polymeric reaction of 8-hydroxyquinoline and thienyl-substituted poly(borylstyrene)[5] or poly(fluorenylborane)[6] and have further succeeded in synthesis of intriguing coordination polymers with quinolate ligands and boron centers embedded in the main chain through boron-induced ether cleavage.[7] Fraser et al. have demonstrated synthesis of boron diketonate-end-functionalized polylactides,[8] poly(ε-caprolactone),[9] and their block copolymers[10] exhibiting interesting phosphorescence by ring-opening polymerization of lactides or ε-caprolactone using boron diketonate with a hydroxyl group as an initiator. We have also reported the synthesis of the π-conjugated polymers integrated organoboron quinolates,[11] aminoquinolate,[12] and diketonate[13] into polymer backbones such as poly(*p*-arylene-ethynylene)s, which are currently one of the most important classes of conjugated polymers used as emitting, charge-transporting, conducting, and sensing materials.[14] Their polymers possess similar properties such as strong fluorescence and efficient energy migration to boron-chelating moieties by extending π-conjugation along the polymer main chain.

4-Difluoro-4-bora-3*a*,4*a*-diaza-*s*-indacene (BODIPY) derivatives are also one of the organoboron dyes[14] and have become the preferred fluorophores in new fluorescent probes that found widespread applications in numerous fields of modern medicine and science.[16] This is a result of their valuable characteristics, such as relatively higher photostability and photoproperties (such as narrower absorption bands, sharper emission, and higher Φ_F, etc.) relative to fluorescein and other organoboron dyes, e.g., boron quinolate and boron diketonate. Although fine-tuning of their valuable characters containing red shift of absorption and emission maxima has been carried out by functionalization of the BODIPY moiety,[14a,b] most studies have focused on low molecules of BODIPY dyes. Previously, we have reported first paper describing preparation of highly fluorescent organoboron polymers with supramolecular self-assembled chain and network structures by incorporating the BODIPY dye into poly(*p*-arylene-ethynylene) backbones.[17] Electronic properties of the poly(*p*-arylene-ethynylene)s displayed higher energy transfer efficiency from π-conjugated linkers to BODIPY moieties, However, no red shift of absorption and emission maxima from extended π-conjugation was observed, because *p*-arylene-ethynylene moieties were directly attached to boron atoms. Recently, to improve our defective electroproperties, Liu et al. have reported synthesis of BODIPY polymeric dyes with emission maxima at 585−683 nm; i.e., the conjugated polymers showed significant extension of π-conjugation by attaching directly to BODIPY cores, with triple-bond[18] or fluorene[19] connections between BODIPY cores and aromatic units. These reports encouraged us to further extend these investigations to design BODIPY-based conjugated polymers with longer wavelength emission, narrower emission band, and higher Φ_F, i.e., near-infrared (NIR)

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conjugated polymers (emission maxima >700 nm),[20] which is of great interest to extend the emission wavelength to NIR region to apply the light-emitting polymers to telecommunications,[21] ionic laser,[22] photovoltaic cells,[23] and light-emitting devices,[24] etc. Herein, a candidate approach is the introduction of a BODIPY core fused aromatic ring, i.e., boron di(iso)indomethene replaced pyrrole by isoindole (high light emitting at 610−730 nm),[25] into a polymer main chain. In this article, we wish to describe the synthesis of high NIR emissive π-conjugated polymers with narrow emission bands by the incorporation of three different aromatic-fused BODIPY monomers into the poly(p-phenylene-ethynylene) backbone.

Experimental Section

Instrumentation. ^{1}H (400 MHz) and ^{11}B (128 MHz) NMR spectra were recorded on a JEOL JNM-EX400 spectrometer. ^{1}H NMR spectra used tetramethylsilane (TMS) as an internal standard in $CHC1_2$, DMSO-d_6, and ^{11}B NMR spectra were referenced externally to $BF_3\cdot OEt_2$ (sealed capillary). Number-average molecular weight (M_n) and molecular weight distribution [weight-average molecular weight/number-average molecular weight (M_w/M_n)] values of all polymers were estimated by size exclusion chromatography (SEC) with a TOSOH 8020 series [a dual pump system (DP-8020), a column oven (CO-8020), and a degasser (SD-8020)] equipped with three consecutive polystyrene gel columns [TOSOH gels: α-4000] and a refractive-index (RI-8020) and an ultraviolet detector (UV-8020) at 40 °C. The system was operated at a flow rate of 1.0 mL/min with chloroform as an eluent. Polystyrene standards were employed for calibration. Fourier transform infrared (FT-IR) spectra were recorded as KBr pellets on a Shimadzu IRrestige-21 spectrometer. UV−vis absorption spectra were recorded on a Shimadzu UV-3600 spectrophotometer, fluorescence emission spectra were measured on a HORIBA Jobin Yvon Fluoromax-4 spectrofluorometer, and fluorescence micrograph on an Olympus IX71 fluorescence microscope.

Materials. 2-Hydroxy-4-iodoacetophenone[26] and 1,4-diethynyl-2,5-dihexadecyloxybenzene[13] were prepared according to the literature. 9,9-Dioctylfluorene-2,7-diboronic acid (Aldrich Chemical Co., 96%), lead(IV) acetate (Wako Chemical Co., 90%), boron trifloride diethyl etherate ($BF_3\cdot OEt_2$, Aldrich Chemical Co.), benzoylhydrazine (Tokyo Kasei Kogyo Co., $>98\%$), 4-methoxybenzoylhydrazine (Tokyo Kasei Kogyo Co., $>98\%$), and 2-methoxybenzoylhydrazine (Aldrich Chemical Co., $>98\%$) were used as received. Tetrahydrofuran (THF) and triethylamine (NEt_3) were purified using a two-column solid-state purification system (Glass Coutour System, Joerg Meyer, Irvine, CA).

Synthesis of (*Z*)-*N'*-(1-(2-Hydroxy-4-iodophenyl)ethylidene)-benzohydrazide (3a). A solution of 1-(2-hydroxy-4-iodophenyl)ethanone (**1**) (4.0 g, 15.3 mmol) and benzylhydrazine (**2a**) (3.15 g, 23.1 mmol) in 1-propanol (20 mL) was stirred at 110 °C for 12 h. After cooling to room temperature, the resulting solid is collected by filtration, washed with 1-propanol, and then dried to give **3a** (5.63 g, 14.8 mmol). The obtained **3a** was used for next reaction without purification. Yield = 97%. ^{1}H NMR (DMSO-d_6): $\delta = 2.47$ (s, 3H, $C_6H_3-(C{=}N-)-CH_3$), 7.26 (d, 1H, $J = 8.28$ Hz, Ar−H), 7.31 (s, 1H, Ar−H), 7.40 (d, 1H, $J = 8.32$ Hz, Ar−H), 7.55 (t, 2H, $J = 7.32$ and 14.6 Hz, Ar−H), 7.63 (t, 1H, $J = 7.32$ and 14.6 Hz, Ar−H), 7.94 (d, 2H, $J = 7.32$ Hz, Ar−H), 11.41 (s, 1H, $\rangle C{=}N-NH-(C{=}O)-$), 13.61 ppm (s, 1H, $-C_6H_3-OH$). HRMS (EI) Calcd for $C_{15}H_{13}O_2N_2$ (M^+): m/z 380.0022. Found: m/z 380.0012.

Synthesis of (*Z*)-*N'*-(1-(2-Hydroxy-4-iodophenyl)ethylidene)-2-methoxybenzohydrazide (3b). 3b was prepared from 2-methoxybenzylhydrazine (**2b**) (3.84 g, 23.1 mmol) in 97% (6.10 g, 14.9 mmol) yield according to the method for **3a**. ^{1}H NMR (DMSO-d_6): $\delta = 2.40$ (s, 3H, $C_6H_3-(C{=}N-)-CH_3$), 3.97 (s, 3H, $-NH-(C{=}O)-C_6H_4-OCH_3$), 7.12 (t, 1H, $J = 7.60$ and 14.8 Hz, Ar−H), 7,24 (t, 2H, $J = 8.40$ and 18.4 Hz, Ar−H), 7.30 (s, 1H, Ar−H), 7.40 (d, 1H, $J = 8.40$ Hz, Ar−H), 7.57 (t, 1H, $J = 7.2$ and 14.4 Hz, Ar−H), 7.83 (d, 1H, $J = 6.4$ Hz, Ar−H), 11.25 (s, 1H, 1H, $\rangle C{=}N-NH-(C{=}O)-$), 13.42 ppm (s, 1H, 1H, $-C_6H_3-OH$). HRMS (EI) Calcd for $C_{16}H_{15}O_3N_2$ (M^+): m/z 410.0127. Found: m/z 410.0122.

Synthesis of (*Z*)-*N'*-(1-(2-Hydroxy-4-iodophenyl)ethylidene)-4-methoxybenzohydrazide (3c). 3c was prepared from 4-methoxybenzylhydrazine (**2c**) (2.91 g, 17.5 mmol) in 99% yield (4.71 g, 11.58 mmol) according to the method for **3a**.^{1}H NMR (DMSO-d_6): $\delta = 2.46$ (s, 3H, $C_6H_3-(C{=}N-)-CH_3$), 3.85(s, 3H, $-NH-(C{=}O)-C_6H_4-OCH_3$), 7.08 (d, 2H, $J = 8.80$ Hz, Ar−H), 7.27 (t, 2H, $J = 8.4$ and 19.6 Hz, Ar−H), 7.39 (d, 1H, $J = 8.00$ Hz, Ar−H), 7.94 (d, 2H, $J = 8.80$ Hz, Ar−H), 11.24 (s, 1H, 1H, $\rangle C{=}N-NH-(C{=}O)-$), 13.66 ppm (s, 1H, 1H, $-C_6H_3-OH$). HRMS (EI) Calcd for $C_{16}H_{15}O_3N_2$ (M^+): m/z 410.0127. Found: m/z 410.0112.

Synthesis of 1-(2-Benzoyl-4-iodophenyl)ethanone (4a). Lead tetraacetate (6.56 g, 14.8 mmol) was added to a suspension of **3a** (4.64 g, 12.2 mmol) in dry THF (110 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 is concentrated by rotary evaporator and purified by silica gel chromatography using $CHCl_3$ as an eluent. Yield = 93% (3.98 g, 11.4 mmol). ^{1}H NMR ($CDCl_3$): $\delta = 2.48$ (s, 3H, $C_6H_3-C({=}O)-CH_3$), 7.43 (t, 2H, $J = 7.56$ and 15.1 Hz, Ar−H), 7.53−7.61 (m, 2H, Ar−H), 7.72 (d, 3H, $J = 8.56$ Hz, Ar−H), 7.94 ppm (d, 1H, $J = 8.0$ Hz, Ar−H). HRMS (EI) Calcd for $C_{15}H_{13}O_2N_2$ (M^+): m/z 349.9804. Found: m/z 349.9801.

Synthesis of 1-(4-Iodo-2-(2-methoxybenzoyl)phenyl)ethanone (4b). 4b was prepared from **3b** (5.0 g, 12.2 mmol) in 95% yield (4.40 g, 11.6 mmol) according to the method for **4a**. ^{1}H NMR ($CDCl_3$): $\delta = 2.38$ (s, 3H, $C_6H_3-C({=}O)-CH_3$), 3.55 (s, 3H, $-C_6H_3-OCH_3$), 6.86 (d, 1H, $J = 8.28$ Hz, Ar−H), 6.97 (t, 1H, $J = 7.89$ and 15.12 Hz, Ar−H), 7.53 (d, 1H, $J = 8.04$ Hz, Ar−H), 7.45 (t, 1H, $J = 7.08$ and 14.16 Hz, Ar−H), 7.59 (d, 1H, $J = 1.48$ Hz, Ar−H), 7.68 (dd, $J = 1.71$ amd 4.03 Hz, Ar−H), 7.78 ppm (dd, 1H, $J = 1.72$ and 4.04 Hz, Ar−H). HRMS (EI) Calcd for $C_{16}H_{13}O_3I$ (M^+): m/z 379.9909. Found: m/z 379.9897.

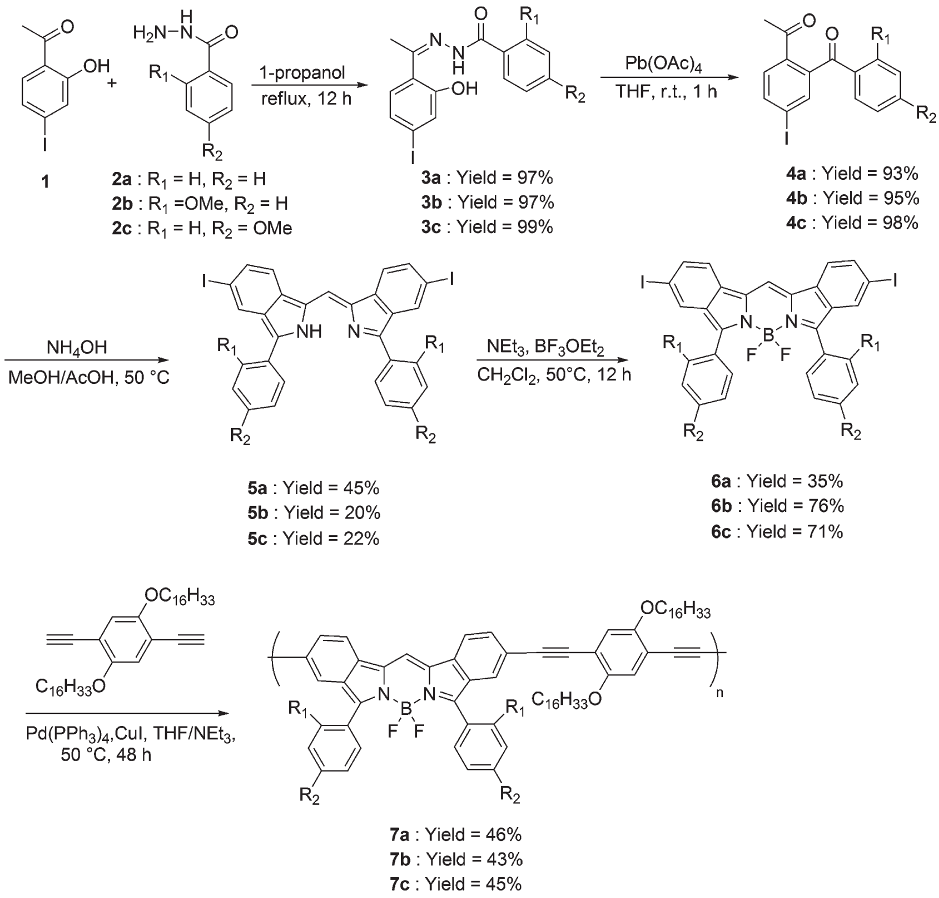
Synthesis of 1-(4-Iodo-2-(4-methoxybenzoyl)phenyl)ethanone (4c). 4c was prepared from **3c** (4.64 g, 11.3 mmol) in 98% yield (4.21 g, 11.1 mmol) according to the method for **4a**. ^{1}H NMR ($CDCl_3$): $\delta = 2.54$ (s, 3H, $C_6H_3-C({=}O)-CH_3$), 3.56 (s, 3H, $-C_6H_3-OCH_3$), 7.12 (d, 2H, $J = 8.40$ Hz, Ar−H), 7.26 (t, 2H, $J = 8.2$ and 19.2 Hz, Ar−H), 7.35 (d, 1H, $J = 8.60$ Hz, Ar−H), 7.82 ppm (d, 2H, $J = 8.20$ Hz, Ar−H). HRMS (EI) Calcd for $C_{16}H_{13}O_3I$ (M^+): m/z 379.9909. Found: m/z 379.9906.

Synthesis of Di(iso)indomethene Ligand (5a). Concentrated NH_4OH (NH_3 content 28−30%, 45 mL) was added to a solution of **4a** (3.78 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 is collected by filtration to crude product. The crude product was purified by silica gel chromatography with $CHCl_3$ as an eluent to give **5a** as a dark blue solid. Yield = 45% (3.15 g, 4.87 mmol). ^{1}H NMR ($CDCl_3$): $\delta = 7.34-7.45$ (m, 6H, Ar−H), 7.52 (s, 1H, Ar−CH=), 7.67 (s, 1H, Ar−H), 7.66−7.82 (m, 3H, Ar−H), 8.22 (s, 1H, Ar−H), 8.21 ppm (s, 2H, Ar−H). HRMS (EI) Calcd for $C_{29}H_{18}I_2N_2$ (M^+): m/z 647.9559. Found: m/z 647.9559.

Synthesis of 5b. 5b was prepared from **4b** (4.11 g, 10.8 mmol) in 20% yield (1.51 g, 2.13 mmol) according to the method for **5a**. ^{1}H NMR ($CDCl_3$): $\delta = 3.76$ (s, 6H, $-OCHH_3$), 7.05 (d, 2H, $J = 8.0$ Hz, Ar−H), 7.12 (t, 2H, $J = 7.2$ and 8.4 Hz, Ar−H), 7.41 (t, 2H, $J = 7.6$ and 15.2 Hz, Ar−H), 7.51 (s, 1H, Ar−CH=), 7.63 (dd, 4H, $J = 8.4$ and 36.0 Hz, Ar−H), 7.86 (d, 3H, $J = 7.6$ Hz, Ar−H), 8.20 ppm (s, 1H, Ar−H). HRMS (EI) Calcd for $C_{31}H_{22}O_2N_2I_2$ (M^+): m/z 707.9771. Found: m/z 707.9776.

Synthesis of 5c. 5c was prepared from **4c** (4.11 g, 10.8 mmol) in 28% yield (2.12 g, 2.99 mmol) according to the method for **5a**. ^{1}H NMR ($CDCl_3$): $\delta = 3.93$ (s, 6H, $-OCH H_3$), 7.09 (d, 4H,

Scheme 1. Synthetic Route to Boron Di(iso)indomethene-Based Conjugated Polymers



J = 8.8 Hz, Ar−*H*), 7.40 (s, 1H, Ar−C*H*=), 7.60 (dd, 4H, J = 8.4 and 21.6 Hz, Ar−*H*), 7.90 (d, 4H, J = 8.8 Hz, Ar−*H*), 8.31 ppm (s, 1H, Ar−*H*). HRMS (EI) Calcd for $C_{31}H_{22}I_2N_2O_2$ (M^+): *m*/*z* 707.9771. Found: *m*/*z* 707.9767.

Synthesis of Boron Di(iso)indomethene Dyes (6a). Dry triethylamine (1.20 mL, 12.3 mmol) was added to a solution of **5a** (0.80 g, 1.23 mmol) in CH_2Cl_2 (500 mL), followed by addition of $BF_3 \cdot OEt_2$ (3.00 mL, 24.6 mmol). After the reaction mixture was stirred at 50 °C for 12 h, it is washed with water. The organic layer is separated, dried over anhydrous magnesium sulfate, and concentrated by rotary evaporator to give a blue solid. The crude product was purified by silica gel chromatography with $CHCl_3$ as an eluent to give **6a** as a deep green solid. Yield = 35% (0.30 g, 0.43 mmol). ^1H NMR ($CDCl_3$): δ = 7.48−7.53 (m, 6H, Ar−H), 7.63 (s, 1H, Ar−C*H*=), 7.67 (s, 1H, Ar−*H*), 7.71−7.78 (m, 3H, Ar−*H*), 7.80 (s, 1H, Ar−*H*), 7.96 ppm (s, 2H, Ar−*H*). ^{13}C NMR ($CDCl_3$): δ = 90.2, 120.5, 125.1, 128.2, 128.6, 129.0, 129.1, 129.2, 130.0, 131.8, 132.5, 137.6 ppm. ^{11}B NMR ($CDCl_3$): δ = 1.47 ppm (t, J = 25.0 and 62.5 Hz). HRMS (EI) Calcd for $C_{29}H_{17}N_2F_2B\,I_2$ (M^+): *m*/*z* 695.9542. Found: *m*/*z* 695.9547. Anal. Calcd for $C_{29}H_{17}N_2F_2B\,I_2$: C, 50.04; H, 2.46; N, 4.02; I, 36.46. Found: C, 50.13; H, 2.75; N, 3.72; I, 36.44.

Synthesis of 6b. 6b was prepared from **5b** (1.50 g, 2.11 mmol) in 76% yield (deep blue solid, 1.22 g, 1.61 mmol) according to the method for **6a**. ^1H NMR ($CDCl_3$): δ = 3.70 and 3.78 (s × 2, 6H, $-C_6H_3-OCH_3$ × 2), 6.97−7.08 (m, 3H, Ar−*H*), 7.43−7.48 (m, 3H, Ar−*H*), 7.59−7.75 ppm (m, 8H, Ar−C*H*= and Ar−*H*). ^{13}C NMR ($CDCl_3$): δ = 55.6, 55.8, 89.1, 111.1, 115.4, 119.3, 120.4, 127.5, 131.4, 131.9, 132.3, 132.8, 133.0, 137.1, 157.7 ppm. ^{11}B NMR ($CDCl_3$): δ = 1.17 ppm (t, J = 25.0 and 50.0 Hz). HRMS (EI) Calcd for $C_{31}H_{21}O_2N_2F_2BI_2$ (M^+): *m*/*z* 755.9754. Found: *m*/*z* 755.9744. Anal. Calcd for $C_{31}H_{21}O_2N_2F_2BI_2$: C, 49.24; H, 2.80; N, 3.70; I, 33.57. Found: C, 48.90; H, 2.73; N, 3.50; I, 33.69.

Synthesis of 6c. 6c was prepared from **5c** (0.18 g, 0.23 mmol) in 71% yield (deep purple solid, 123 mg, 0.16 mmol) according to the method for **6a**. ^1H NMR ($CDCl_3$): δ = 3.89 (s, 6H, $-C_6H_3-OCH_3$), 7.04 (d, 4H, J = 6.80 Hz, aromatic proton), 7.61 (s, 1H, Ar−C*H*=), 7.63 (s, 1H, Ar−*H*), 7.67−7.69 (m, 2H, Ar−*H*), 7.71 (s, 1H, Ar−*H*), 7.76 (d, 4H, J = 8.80 Hz, Ar−*H*), 7.98 ppm (s, 2H, Ar−*H*). ^{13}C NMR ($CDCl_3$): δ = 55.3, 89.7, 114.1, 120.5, 122.8, 127.8, 131.8, 132.4, 132.6, 132.7, 137.3, 150.9, 160.9 ppm. ^{11}B NMR ($CDCl_3$): δ = 1.56 ppm (t, J = 37.5 and 62.5 Hz). HRMS (EI) Calcd for $C_{31}H_{21}O_2F_2N_2BI_2$ (M^+): *m*/*z* 755.9754. Found: *m*/*z* 755.9750. Anal. Calcd for $C_{31}H_{21}O_2N_2F_2BI_2$: C, 49.24; H, 2.80; N, 3.70; I, 33.57. Found: C, 49.21; H, 2.68; N, 3.46; I, 33.51.

Synthesis of Polymer 7a. Triethylamine (0.75 mL) was added to a solution of **6a** (52.2 mg, 0.075 mmol), 1,4-diethynyl-2,5-dihexadecyloxybenzene (45.5 mg, 0.075 mmol), $Pd(PPh_3)_4$ (4.33 mg, 3.75 μmol), and CuI (0.71 mg, 3.75 μmol) in THF (1.5 mL) at 50 °C under a nitrogen atmosphere. After the mixture was stirred at 50 °C for 48 h, the solvent was evaporated out *in vacuo*. The residue was extracted with $CHCl_3$, washed with 10% ammonia−water and then water, and dried over $MgSO_4$; the volatile products were evaporated. The residue was dissolved in a small amount of $CHCl_3$ and poured into a large excess of methanol to precipitate a polymer. The polymer was collected by filtration with suction, further washed with acetone, and then dried under vacuum at 60 °C for 12 h. **7a** was obtained as a deep green blue solid. Yield = 46% (72.0 mg, 68.8 μmol). M_n = 8200, M_w/M_n = 1.94. ^1H NMR ($CDCl_3$): δ = 0.62−0.85 (6H, CH_3 × 2), 0.85−1.35 (48H, $-CH_2-$ × 24), 1.36−1.60 (4H, $-CH_2-$ × 2), 1.63−1.89 (4H, $-CH_2-$ × 2), 3.77−4.03 (4H, $-OCHH_2-$ × 2), 6.68−7.96 ppm (19H, Ar−*H*). ^{13}C NMR ($CDCl_3$): δ = 14.1, 22.7, 25.9, 29.4, 29.7, 29.7, 31.9, 69.3, 86.5, 95.1, 113.9, 115.2, 118.9, 120.5, 127.4, 128.3, 129.9, 130.2, 130.5, 131.9, 132.5, 133.0, 137.5,

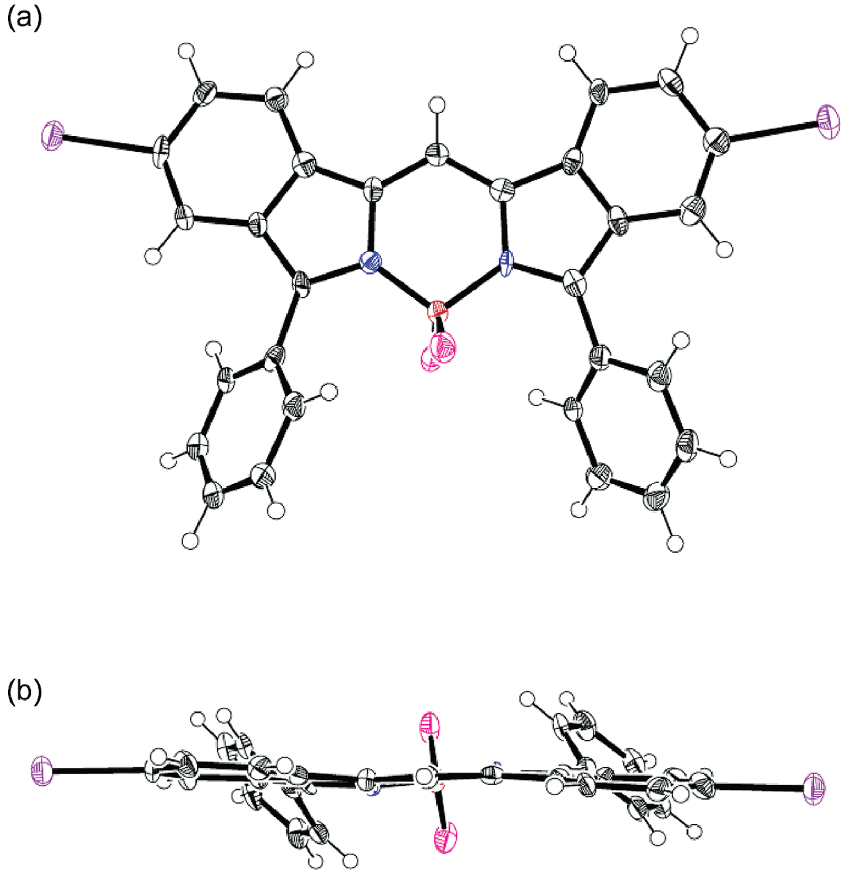


Figure 1. X-ray crystal structures of **6a** (a) top view and (b) side view with thermal ellipisoids drawn to the 50% probability level.

152.6, 153.7 ppm. ^{11}B NMR (CDCl$_3$): δ = 1.56 ppm. IR (KBr): ν = 3439, 2922. 2850, 1618, 1589, 1560, 1541, 1508, 1458, 1389, 1263, 1204, 1157, 1107 cm^{-1}. Anal. Calcd for $(C_{71}H_{85}O_2N_2F_2BF_2)_n$: C, 81.43; H, 8.18; N, 2.67. Found: C, 79.55; H, 8.03; N, 2.67.

Synthesis of Polymer 7b. 7b was prepared from **6b** with 1, 4-diethynyl-2,5-dihexadecyloxybenzene in 43% yield (72.0 mg, 65.0 μmol), according to the method for polymer **7a**. M_n = 7600, M_w/M_n = 2.12. ^{1}H NMR (CDCl$_3$): δ = 0.74−0.86 (6H, CH_3 × 2), 0.98−1.34 (48H, −CH_2− × 24), 1.34−1.62 (4H, −CH_2− × 2), 1.63−1.85 (4H, −CH_2− × 2), 3.58−3.66 and 3.68−3.73 (6H, −OCH_3 × 2), 3.84−3.99 (4H, −OCH_2− × 2), 6.79−7.08 (6H, Ar−H), 7.30−7.87 ppm (11H, Ar−H). ^{13}C NMR (CDCl$_3$): δ = 14.1, 22.7, 25.9, 29.3, 29.4, 29.6, 29.7, 31.9, 55.7, 56.1, 69.6, 85.8, 95.7, 111.0, 115.4, 116.8, 117.9, 118.8, 119.6, 120.4, 127.4, 127.6, 131.2, 131.9, 132.4, 132.7, 153.6, 157.8 ppm. ^{11}B NMR (CDCl$_3$): δ = 1.27 ppm. IR (KBr): ν = 3442, 2924, 2852, 2814, 1614, 1589, 1562, 1502, 1266, 1203, 1155, 1102 cm^{-1}. Anal. Calcd for $(C_{71}H_{89}O_2N_2F_2BF_2)_n$: C, 79.18; H, 8.10; N, 2.53. Found: C, 78.23; H, 7.89; N, 2.22.

Synthesis of Polymer 7c. 7c was prepared from **6c** with 1, 4-diethynyl-2,5-dihexadecyloxybenzene in 45% yield (75.0 mg, 67.7 μmol), according to the method for polymer **7a**. M_n = 8100, M_w/M_n = 2.32. ^{1}H NMR (CDCl$_3$): δ = 0.74−0.94 (6H, CH_3 × 2), 0.97−1.41 (48H, −CH_2− × 24), 1.42−1.64 (4H, −CH_2− × 2), 1.70−1.93 (4H, −CH_2− × 2), 3.81−3.93 (6H, −OCH_3 × 2), 3.93−4.10 (4H, −OCH_2− × 2), 6.72−7.15 (6H, Ar−H), 7.43−8 ppm (11H, Ar−H). ^{13}C NMR (CDCl$_3$): δ = 14.1, 22.7, 26.0, 29.4, 29.4, 29.7, 31.9, 55.3, 69.6, 86.2, 96.2, 113.9, 116.8, 118.9, 120.2, 123.0, 124.1, 127.8, 128.4, 130.4, 131.9, 132.1, 132.9, 152.5, 153.8, 160.9 ppm. ^{11}B NMR (CDCl$_3$): δ = 1.66 ppm. IR (KBr): ν = 3412, 2924, 2853, 1611, 1598, 1504, 1454, 1439, 1395, 1255, 1206, 1159, 1139, 1107 cm^{-1}. Anal. Calcd for $(C_{71}H_{89}O_2N_2F_2BF_2)_n$: C, 79.18; H, 8.10; N, 2.53. Found: C, 75.68; H, 7.97; N, 2.11.

Results and Discussion

Synthesis and Characterization. The synthetic route toward the BODIPY monomers fused bis-iodophenyl groups, and the polymers are outlined in Scheme 1. A variety of aryl groups, phenyl, *o*-methoxyphenyl, and *p*-methoxyphenyl groups were introduced to boron di(iso)indomethene monomers at the position adjacent to nitrogen atoms in the pyrrole ring to extend further conjugation length of the monomers. First, the di(iso)indomethene ligands **5a−c** were prepared via the condensation of ammonia and substituted 2-acetophenones **4a−c**, which were obtained from 2-hydroxy-4-iodo-acetophenone and various hydrazines. These were treated with boron trifluoride to give boron di(iso)indomethene-based monomers **6a−c** in satisfactory yields. Further, a single crystal of **6a** was obtained by recrystallization from a mixed solvent of CH_2Cl_2/hexane. X-ray analysis indicated that **6a** forms tetracoordination state on the central boron atom (Figure 1a and Table S1) and has high planarity of the boron-coordinated ligand moiety (Figure 1b). The structures of all the intermediates and the final monomers were confirmed by ^{1}H NMR, ^{13}C NMR, ^{11}B NMR, and electron ionization mass spectroscopies or elemental analysis.

The polymerization was accomplished by palladium-catalyzed Sonogashira reaction of **6a−c** and 1,4-diethynyl-2,5-dihexadecyloxybenzene in a mixed solvent of THF/NEt_3 in the presence of $Pd(PPh_3)_4$ and Cu(I)I. After 48 h at 50 °C, the polymers were precipitated into methanol and further acetone in 43−46% yields. All polymers synthesized were fusible and soluble in common organic solvents including THF, benzene, toluene, $CHCl_3$, and CH_2Cl_2, etc. The size-exclusion chromatography (SEC) in $CHCl_3$ toward polystyrene standards revealed the number-average molecular weights (M_n) and the molecular distribution (M_w/M_n) of

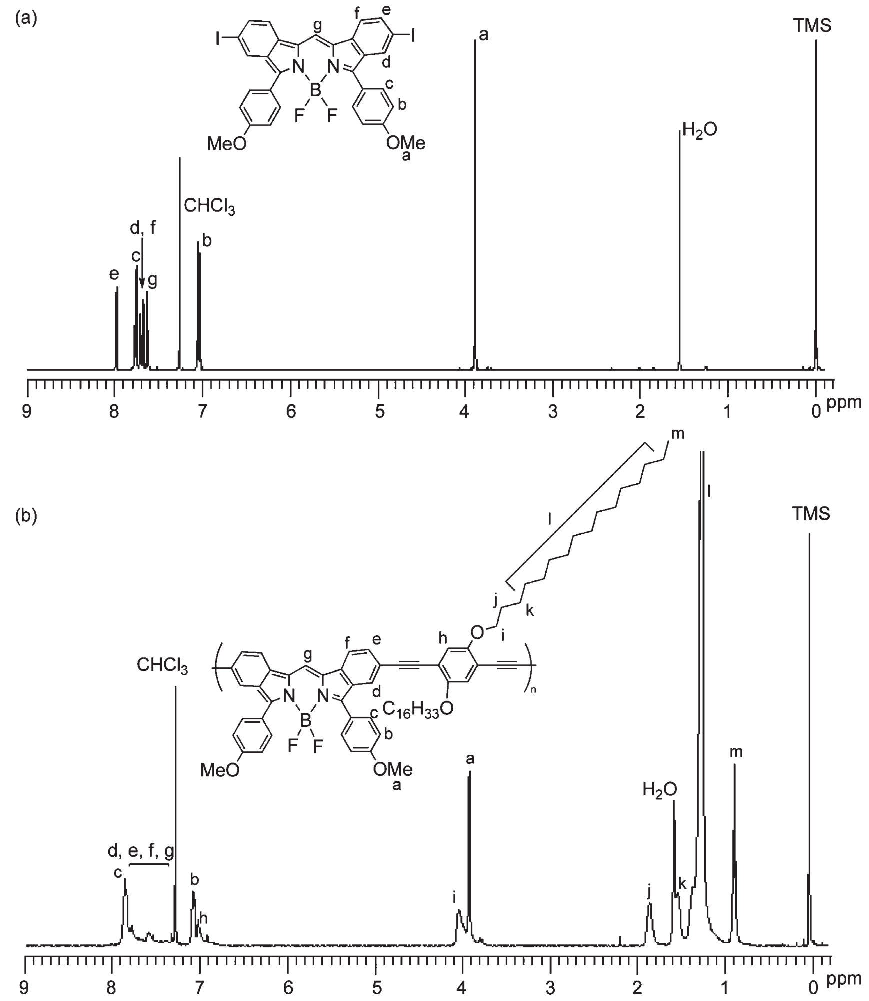


Figure 2. ^{1}H NMR spectra of **6c** and **7c** in $CDCl_3$.

8200 and 1.94, 7900 and 2.12, and 8100 and 2.32 (**7a**, **7b**, and **7c**, respectively). The degrees of polymerization (DPs), estimated by M_n from SEC, of the polymers were 7.1−7.8. The chemical structures of the polymers were confirmed by ^{1}H NMR, ^{11}B NMR, and IR spectroscopies, besides elemental analysis. All the purified polymerization products gave satisfactory spectroscopic data corresponding to their expected molecular structures. A typical example of the ^{1}H NMR spectra of **6c** and **7c** is shown in Figure 2, which sufficiently supports the structure of the products by the assignments of the signals as described in the Experimental Section. As expected, the resonance peaks in the ^{1}H NMR spectra of polymers are broader than those of monomers due to part to their longer rotational correlation times, indicating that the monomers had been polymerized successfully. Further, in the ^{1}H NMR spectra of **6b** and **7b** the two signals assignable to *o*-methoxyphenyl groups in **6b** and **7b** were observed at around 3.70−4.00 ppm, whereas ligand **5b** is only one signal assigned to *o*-methoxyphenyl groups at 3.76 ppm, meaning the presence of isomers originating from steric hindrance between two fluoride atoms and two *o*-methoxyphenyl groups.

UV−vis Absorption and Photoluminescence. The UV−vis absorption and photoluminescence (PL) properties of the monomers **6a**−**c** and polymers **7a**−**c** are presented in Table 1. Figure 3a shows the absorption spectra of the monomers and polymers in $CHCl_3$ solution (1.0×10^{-5} M). The absorptions of the monomers are characterized by strong $S_0 \rightarrow S_1$ ($\pi \rightarrow \pi^*$) transition at around 670−702 nm and weaker broad bands at a shorter wavelength around 375 nm ascribed to the $S_0 \rightarrow S_2$ ($\pi \rightarrow \pi^*$) transition. The absorption maximum (λ_{ab}) of monomer **6c** was shifted to longer wavelength than those of **6a** and **6b** due to extension of conjugation length by *p*-methoxyphenyl group as electron-donating group. In contrast, the absorption maximum of **6b** with *o*-methoxyphenyl group was blue-shifted compared with that of **6a**, probably causing no extension of conjugation length due to rectangular state between *o*-methoxyphenyl groups and ligand core in **6b** by steric hindrance (discussion later). However, the molar absorption coefficient (ε) of **6b** was higher than those of **6a** and **6c**. The absorptions of the polymers were observed at strong $\pi \rightarrow \pi^*$ transition at around 691−720 nm and weaker bands at shorter wavelength at around 440 nm attributable to $\pi \rightarrow \pi^*$ transition of the *p*-phenylene-ethynylene segments. Introduction of the monomers **6a**−**c** into the poly(*p*-phenylene-ethynylene) segments led to red shifts of the UV absorption (**7a**: 24 nm; **7b**: 24 nm; **7c**: 27 nm). The red-shifted absorptions of the polymers in the order were **7c** > **7a** > **7b** as well as the results of the monomers. Moreover, the absorption peaks of the polymers become broader than the monomers as a result of the extended π-conjugation. In the PL spectra (Figure 3b), the maxima (excited at λ_{ab}) of **6a**−**c** were 673−702 nm; that is, they emit in the range from deep-red to NIR region. In contrast, the polymers **7a**−**c** exhibit obvious bathochromic shifts of the PL maxima relative to monomers (**7a**: 22 nm; **7b**:

18 nm; **7c**: 18 nm), indicating efficient extension of π-conjugation along the *p*-phenylene-ethynylene linker. Although absolute quantum yields (Φ_F) of the polymers decreased in comparison with those of the monomers, their $_F$ was enough high in the range from deep-red to NIR region (Φ_F = 33−49%). Further, the molar absorption coefficients of the polymers were very large.

Table 1. UV−vis Absorption and Photoluminescence Data for Monomers 6a−c and Polymers 7a−c in CHCl$_3$ Solution[a]

compound	λ_{ab} (nm)	ε ($\times 10^5$ M^{-1} cm^{-1})	λ_{em}[b] (nm)	Φ_F[c] (%)
6a	653	1.55	683	56
6b	638	2.09	673	62
6c	667	2.05	702	72
7a	677	1.42	705	33
7b	662	2.02	691	49
7c	694	2.14	720	38

[a] CHCl$_3$ (1.0 × 10^{-5} M). [b] Excited at absorption maxima (λ_{ab}). [c] Φ_F = absolute quantum yield (excited at λ_{ab}).

Molecular Orbital Calculations. To confirm assignments of the absorption bands for the polymers **7a−c**, especially relationship between **7a** and **7b**, we performed the theoretical calculation of the model compounds **8a−c**, which were designed by the Gaussian 03 suit of programs,[27] using the density-functional theory (DFT) method at the B3LYP/6-31G(d,p)//B3LYP/6-31G(d,p) level of theory. Figure 4 displays the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of **8a−c**. The LUMO of the model compounds is mainly located on the boron di(iso)indomethene ligand, and the HOMO is localized not only on the ligand but also on the *p*-phenylene-ethynylene moieties. However, the LUMO and HOMO of **8b** are not almost on the whole of *o*-methoxyphenyl groups in the ligand due to orthogonal situation between *o*-methoxyphenyl groups and ligand by steric hindrance, meaning lower extended π-conjugation of monomer **6b** and **7b** relative to other monomers and polymers. Further, the HOMO−LUMO band gap of **8b** is wider than that

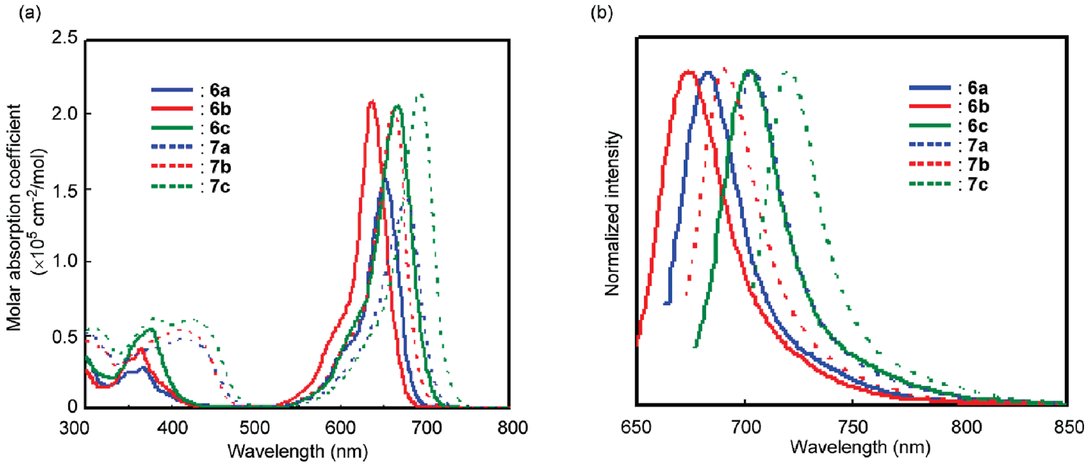


Figure 3. (a) UV−vis absorption spectra and (b) normalized photoluminescence spectra of **6a−c** and **7a−c** in CHCl$_3$ (1.0 × 10^{-5} mol/L).

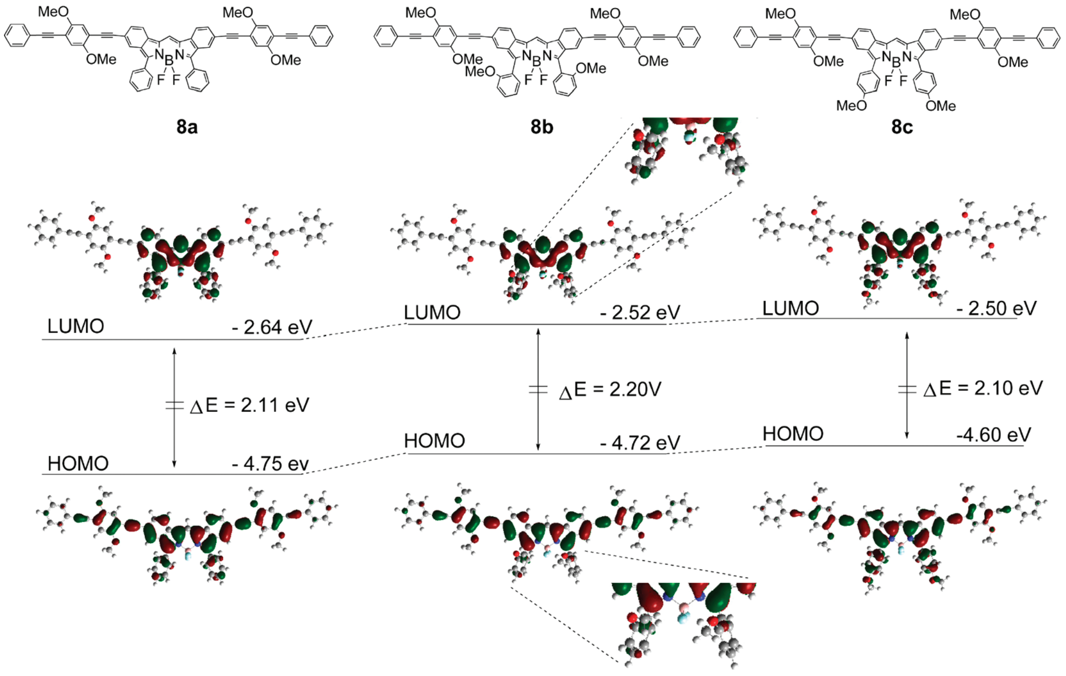


Figure 4. Structures and molecular orbital diagrams for the LUMO and HOMO of designed model compounds **8a−c** (B3LYP/6-31G(d,p)//B3LYP/6-31G(d,p)).

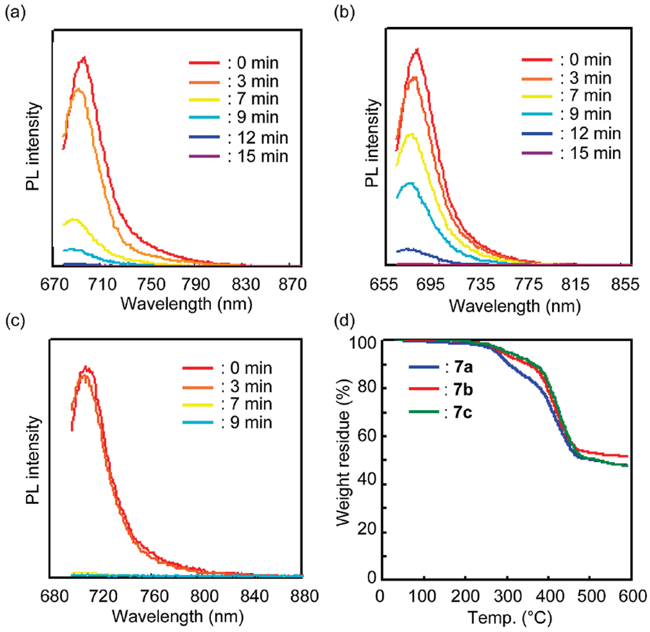


Figure 5. Photoluminescence spectra of (a) **7a**, (b) **7b**, and (c) **7c** under continuous UV irradiation (254 nm) in 1,2-dichloropropane ($c = 1.0 \times 10^{-5}$ M) and (d) TGA profiles of **7a**–**c**.

of **8a** and **8c**, meaning higher bathochromic shift of **7a** relative to that of **7b**. Accordingly, the order of the absorption maxima of the polymers **7a**–**c** is excellently identical to that of the band gaps of the designed model compounds; i.e., the λ_{ab} is in the order **7c** > **7a** > **7b**, and the band gaps are in the order **8c** < **8a** < **8b**.

Photostabilities and Thermal Stabilities. Figures 5a–c show photostabilities of the obtained polymers **7a**–**c** in 1,2-dichloropropane. The photo-oxidation studies were performed by continuous UV irradiation using a 4 W steady-state UV lamp (254 nm) as the irradiation source under aerobic conditions, and monitoring of decrease of PL spectra provided their photodecomposition behaviors. Although the decrease of PL intensity of all polymers was slight after 3 min, an obvious difference of their PL intensity was observed after 7 min. The photostability of **7b** was high enough as compared with that of **7a**. In contrast, the PL intensity of **7b** decreased rapidly and almost disappeared. Accordingly, the photostabilities of the polymers were on the order of **7b** > **7a** > **7c**, analogizing with the order of their emission and absorption wavelength. These results might consider that the photostabilities of the polymers are related to electronic density and/or steric hindrance of the substituents. Further, the PL intensity of all polymers retained durably until 1 week under continuous UV irradiation (365 nm), indicating that the obtained polymers possess high photostabilities toward long wavelength irradiation.

Thermal degradation behaviors of the obtained polymers were investigated by thermogravimetric anaysis (TGA). The TGA profiles for the polymers **7a**–**c** are shown in Figure 5d. The 5 and 10% weight loss temperature (T_5 and T_{10}) for **7b** were 289 and 354 °C, whereas for **7a**, the T_5 and T_{10} values were 279 and 305 °C, respectively, lower than those of **7b**. In comparison with **7b** and **7c**, the T_5 and T_{10} values of **7c** increased to 303 and 366 °C. These data support that the polymers having methoxy groups take on a thermodynamically stable structure. The interrelationships between thermal stability and substituent position of methoxy groups in the resulting polymers will be investigated.

Conclusion

Through the use of palladium-catalyzed Sonogashira couplings, three light-emitting conjugated copolymers with alternating *p*-phenylene-ethynylene and boron di(iso)indomethene units were successfully prepared. The introduction of the boron di(iso)indomethene skeleton into the polymer backbone was confirmed by chemical and photophysical characterizations. The incorporation of the indomethene monomers into *p*-phenylene-ethynylene main chain led to red shifts in UV-absorption and PL spectra by extended π-conjugation of the copolymers in comparison with indomethene monomers. Consequentially, three conjugated copolymers emitted intensely in the range from deep-red to NIR region ($\Phi_F = 33–49\%$). The photostabilities of the polymers were examined by monitoring decrease of the PL spectra under continuous UV irradiation using a UV lamp under aerobic conditions. As far as we know, this is the first finding of the synthesis of aromatic ring-fused BODIPY-based conjugated polymers with both intense NIR luminescence and the narrow emission bands. Currently, further studies are underway to design NIR luminescence conjugated polymer sharing both intense NIR-emitting monomers with longer wavelength such as boron azadipyrromethene (aza-BODIPY) and conjugated linker skeleton with narrower band gap.

Supporting Information Available: CIF file and Table S1 of monomer **6a**. This material is available free of change via the Internet at http://pubs.acs.org.

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