Synthesis and Optical Properties of Red and Deep-Red Emissive Polymeric and Copolymeric BODIPY Dyes

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Deep-red emissive polymeric BODIPY dyes (polymers **A** and **B**), poly(2,6-BODIPY-ethynylene)s, were prepared by palladium-catalyzed Sonogashira polymerization of 2,6-diiodo-functionalized BODIPY monomers with 2,6-diethynyl-functionalized BODIPY monomers. Poly(2,6-BODIPY-ethynylene)s emit in the deep-red region with emission spectral maxima at around 680 nm and exhibit significant red shifts (up to 163 and 172 nm) of both absorption and emission maxima compared with their initial BODIPY dyes due to significant extension of π-conjugation. Red emissive copolymeric BODIPY dyes (polymers **C**, **D**, and **E**) were also prepared by palladium-catalyzed Sonogashira polymerization of a diethynyl-functionalized BODIPY monomer with 9,9-bis(6′-(hexylthio)hexyl)-2,7-diiodo-9H-fluorene, 1,4-diiodo-2,5-didecyloxybenzene, and 2,5-diiodo-3-decylthiophene, respectively. Incorporation of different band gap monomer units into poly(2,6-BODIPY-ethynylene)s resulted in copolymers with a range of emission wavelengths from 641 to 664 nm. The fluorescence lifetimes of these polymers (polymers **A**−**D**) are from 2.8 to 3.8 ns except the copolymer with thiophene moieties (polymer **E**), which displays a much shorter lifetime of 0.23 ns with low fluorescence quantum yield due to efficient intersystem crossing induced by the heavy atom effect of sulfur.

Introduction

4,4′-Difluoro-4-bora-3a,4a-diaza-*s*-indacene (BODIPY) dyes have received renewed interest for promising applications in light-harvesting systems,[1] biological probes,[2] supramolecular fluorescent gels,[3] solar cells,[4] and ion sensing and signaling[5] because of their many distinctive and desirable properties such as high absorption coefficients, narrow absorption bands, sharp emissions, high fluorescence quantum yields, and excellent chemical and photo stabilities.[6−8] The optical properties of BODIPY dyes have been fine-tuned by functionalization.[6−8] The number and nature of the substituents have resulted in significant red-shifts of their absorption and emission maxima.[6−8] However, most reported studies have focused on small molecules of BODIPY dyes.[6−8] Fluorescent conjugated polymers with BODIPY backbones are expected to combine the unique properties of both BODIPY dyes and conjugated polymers into one package for a variety of potential applications. There is only one interesting paper describing incorporation of the BODIPY unit into poly(*p*-phenylene ethynylene) and poly(fluorene-ethynylene) backbones.[9] All these polymers showed nearly identical emission maxima at 532 nm, which is the same emission peak of typical BODIPY dyes,[9] because *p*-phenylene ethynylene or fluorene ethynylene units were attached to boron atoms at positions 4 and 4′ but not to dipyrromethene cores (Scheme 1), which may prevent phenylene−ethynylene or fluorene−ethynylene units from π-conjugating to BODIPY cores as replacement of the usual fluorine atoms with ethynylaryl subunits does not obviously change absorption and emission spectral maxima of BODIPY dyes.[10−12] Our hypothesis is that palladium-catalyzed Sonogashira polymerization of BODIPY dyes at positions 2 and 6 will allow significant extension of π-conjugation of BODIPY dyes and result in new kinds of rigid linear conjugated polymers, red and deep-red BODIPY polymeric dyes (Scheme 2).

Scheme 1. Chemical Structure of BODIPY Core

In this article, we report new deep-red emissive polymeric BODIPY dyes with triple-bond connections between BO-

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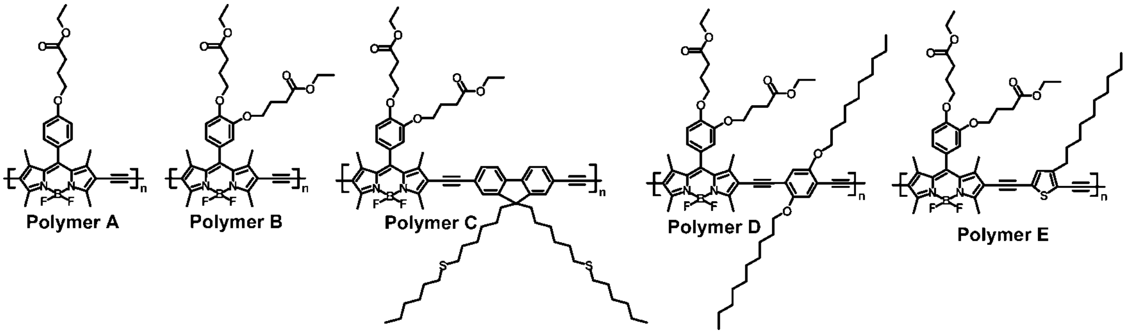
Scheme 2. Chemical Structures of Red and Deep-Red Emissive Polymeric BODIPY Dyes



DIPY cores at positions 2 and 6 (polymers **A** and **B**) and red emissive copolymeric BODIPY dyes with triple-bond connections between BODIPY cores and different band gap aromatic units (polymers **C**, **D**, and **E**, Scheme 2). Poly(2,6-BODIPY-ethynylene)s (polymers **A** and **B**) emit in the deep-red region at around 680 nm and display significant red shifts (up to 163 and 172 nm) of both absorption and emission spectral maxima, respectively, compared with their initial BODIPY dyes because of significant extension of π-conjugation (Scheme 2). Incorporation of different band gap units such as fluorene, phenylene, and thiophene into poly(2,6-BODIPY-ethynylene)s efficiently tune the fluorescence of BODIPY-based conjugated copolymers with different red emissions. These results further confirm our hypothesis. This approach offers a general and facile approach to tune the fluorescence of BODIPY-based conjugated polymers with red and deep-red emission.

Experimental Section

Instrumentation. ^{1}H NMR and ^{13}C NMR spectra were taken on a 400 MHz Varian Unity Inova spectrophotometer instrument. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$, and chemical shifts (δ) are given in ppm relative to solvent peaks (^{1}H, δ 7.26; ^{13}C, δ 77.3) as internal standard. UV spectra were taken on a Hewlett-Packard 8452A Diode Array UV−visible spectrophotometer. Fluorescence spectra were recorded on a Spex Fluorolog 1681 0.22m steady-state fluorometer. Fluorescence quantum yields of BODIPY dyes and polymers were measured in methylene chloride and calculated by using fluorescein excited at 490 nm in 0.1 N NaOH as the reference (quantum efficiency, $\phi_n = 85\%$).[13−16] Fluorescence lifetimes were measured on a GL-3300 Nitrogen Laser laserstrobe PTI instrument and analyzed using FeliX32 software. Molecular weights of the polymers were determined by gel permeation chromatography (GPC) by using a Waters Associates model 6000A liquid chromatograph. Three American Polymer Standards Corp. ultrastyragel columns in series with porosity indices of 10^3, 10^4, and 10^5 Å were used and housed in an oven thermostatted at 30 °C. The mobile phase was HPLC grade THF which was filtered and degassed by vacuum filtration through a 0.5 μm fluoropore filter prior to use. The polymers were detected by a Waters Model 440 ultraviolet absorbance detector at a wavelength of 254 nm and a Waters Model 2410 refractive index detector. Molecular weights were determined relative to polystyrene standards.

Materials. Unless otherwise indicated, all reagents and solvents were obtained from commercial suppliers (Aldrich, Sigma, Fluka, Acros Organics, Fisher Scientific, Lancaster) and were used without further purification. Air- and moisture-sensitive reactions were conducted in oven-dried glassware using a standard Schlenk line or drybox techniques under an inert atmosphere of dry nitrogen. 9,9-Bis-(6′-bromohexyl)-2,7-diido-9H-fluorene,[17] 1,4-diiodo-2,5-didecyloxybenzene (**7b**),[18] and 2,5-diiodo-3-decylthiophene (**7c**)[19,20] were prepared according to the reported procedures.

Ethyl 4-(4-Formylphenoxy)butanoate (1a)**.** When 150 mL of degassed DMF was added to a 500 mL three-neck round-bottom flask containing 4-hydroxybezaldehyde (40.9 mmol, 5 g), ethyl 4-bromobuterate (49.1 mmol, 9.57 g), and K_2CO_3 (122 mmol, 16.8 g) under a nitrogen atmosphere, the mixture was stirred for 4 h at 80 °C under a nitrogen atmosphere. After completion of the reaction (which was monitored by TLC), the reaction mixture was concentrated under reduced pressure. The residue was dissolved in 50 mL of EtOAc and washed twice with water and saturated NaCl solution. The organic layer was collected, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The resulting crude product was purified by silica gel column chromatography using hexane/EtOAc (70/30, v/v) to obtain white solid (9.36 g, 97%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.85 (s, 1H), 7.80 (d, $J = 8.8$ Hz, 2H), 6.99 (d, $J = 8.8$ Hz, 2H), 4.12 (q, $J = 7.2$ Hz, 2H), 4.07 (t, $J = 6.0$ Hz, 2H), 2.50 (t, $J = 7.2$ Hz, 2H), 2.12 (q, $J = 6.4$, 2H), 1.26 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.9, 173.2, 164.1, 132.2, 130.2, 114.9, 67.3, 60.7, 30.8, 24.6, 14.4.

BODIPY Dye 3a. Ethyl 4-(4-formylphenoxy)butanoate (**1a**) (8.72 mmol, 2.07 g) and 2,4-dimethylpyrrole (17.44 mmol, 1.66 g) were dissolved in 1000 mL of dry CH_2Cl_2 in a 2000-mL three-neck flask. Eight drops of trifluoroacetic acid (TFA) were added to the reaction mixture, and the resulting mixture was stirred in the dark for 12 h under nitrogen atmosphere at room temperature. After the complete consumption of aldehyde (**1a**) (which was monitored by TLC), DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) (8.72 mmol 1.974 g) in 10 mL of CH_2Cl_2 was added to the reaction mixture. When the mixture was stirred for 30 min, 17 mL of diisopropylethylamine (DIEA) and 17 mL of $BF_3 \cdot OEt_2$ were added to the mixture. After the mixture was further stirred for 30

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min, it was concentrated to 200 mL and filtered. The filtrate was washed twice with water and brine solution, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by column chromatography using hexane/EtOAc (90/10 to 70/30, v/v) to obtain a dark brown crystalline solid (1.51 g, 38%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13 (d, $J =$ 8.4 Hz, 2H), 6.96 (d, $J =$ 8.4 Hz, 2H), 5.95 (s, 2H), 4.14 (q, $J =$ 7.2 Hz, 2H), 4.04 (t, $J =$ 6.2 Hz, 2H), 2.54−2.51 (m, 8H), 2.15−2.11 (m, 2H), 1.40 (s, 6H), 1.25 (t, $J =$ 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.3, 159.6, 155.4, 143.3, 142.0, 132.0, 129.4, 127.3, 121.2, 115.2, 67.0, 60.67, 30.9, 24.8, 14.8, 14.4. IR: 2954, 2922, 2970, 1736, 1609, 1542, 1514, 1464, 1441, 1408, 1375, 1365, 1309, 1281, 1261, 1239, 1191, 1179, 1153, 1090, 1043, 937, 828, 802,763, 703 cm^{-1}. ESI-MS: M$^+$ ($C_{25}H_{29}BF_2N_2O_3$) calcd, *m/z* = 454.2; found, *m/z* = 454.9. It shows absorption maximum at 501 nm and emission maximum at 510 nm in CH_2Cl_2 solution.

BODIPY Dye 4a. When iodic acid (6.13 mmol, 1.08 g) in 5 mL of water was added dropwise to the ethanol solution (50 mL) containing compound **3a** (3.1 mmol 1.4 g) and iodine (6.7 mmol 0.85 g) over 30 min, the mixture was stirred for 2 h.[14] After the completion of the reaction, the mixture was concentrated under reduced pressure, dissolved in CH_2Cl_2, and washed twice with water and saturated saline solution. The organic layer was collected, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by column chromatography to yield **4a** as red crystals (2.1 g, 98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11 (d, $J =$ 8.4 Hz, 2H), 6.99 (d, $J =$ 8.4 Hz, 2H), 4.15 (q, $J =$ 7.2 Hz, 2H), 4.06 (t, $J =$ 6.0 Hz, 2H), 2.62 (s, 6H), 2.54 (t, $J =$ 6.0, 2H), 2.17−2.13 (m, 2H), 1.42 (s, 6H), 1.26 (t, $J =$ 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.3, 160.0, 156.8, 145.5, 141.7, 131.9, 129.3, 126.9, 115.5, 85.7, 67.2, 60.7, 30.9, 24.8, 17.4, 16.2, 14.5. IR: 2961, 2899, 1720, 1605, 1538, 1509, 1464, 1431, 1398, 1344, 1310, 1296, 1263, 1225, 1177, 1073, 1042, 1000, 916, 837, 763, 705 cm^{-1}. ESI-MS: M$^+$ ($C_{25}H_{27}BF_2I_2N_2O_3$) calcd, *m/z* = 706.0; found, *m/z* = 705.6. It shows an absorption maximum at 533 nm and emission maximum at 548 nm in CH_2Cl_2 solution.

BODIPY Dye 5a. BODIPY dye **4a** (1.69 mmol, 1.2 g), CuI (0.02 mmol, 0.004 g), and $Pd(PPh_3)_2Cl_2$ (0.02 mmol, 0.015 g) were added to a 100-mL three-neck round-bottom flask under a nitrogen atmosphere. When 20 mL of anhydrous degassed THF, 20 mL of anhydrous diisopropylamine, and trimethylsilylacetylene (5.0 mmol, 0.49 g) were added to the flask, the mixture was stirred under reflux for 4 h. After the completion of the reaction (which was monitored by TLC), the reaction mixture was concentrated and dissolved in 50 mL of CH_2Cl_2 and washed twice with water and saturated saline solution. The organic layer was collected, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The product was purified by silica gel column chromatography using hexane/EtOAc (95/5 to 80/20, v/v) to yield orange-red solid (0.91 g, 84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 (d, $J =$ 8.4 Hz, 2H), 6.98 (d, J = 8.4 Hz, 2H), 4.15 (q, $J =$ 7.2 Hz, 2H), 4.05 (t, $J =$ 6.0 Hz, 2H), 2.60 (s, 6H), 2.54 (t, $J =$ 6.0, 2H), 2.16−2.13 (m, 2H), 1.48 (s, 6H), 1.26 (t, $J =$ 6.8 Hz, 3H) 0.19 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.3, 159.9, 158.7, 145.1, 143.1, 131.6, 129.3, 126.7, 116.3, 115.4, 101.8, 97.4, 67.1, 60.7, 30.9, 24.8, 14.4, 13.8, 0.28. IR: 2955, 2923, 2152, 1737, 1609, 1530, 1472, 1393, 1366, 1318, 1290, 1247, 1198, 1174, 1086, 1048, 1001, 946, 930, 765, 703 cm^{-1}. ESI-MS [M]$^+$ ($C_{35}H_{45}BF_2N_2O_3Si_2$) calcd, *m/z* = 646.3; found, *m/z* = 647.4. It shows absorption maximum at 553 nm and emission maximum at 569 nm in CH_2Cl_2 solution.

BODIPY Dye 6a. When BODIPY dye **5a** (0.77 mmol, 0.50 g) was dissolved in degassed THF (8 mL) in a 50-mL flask at −70 °C, tetrabutylammonium fluoride (TBAF) (3.1 mmol, 3 mL of 1 M solution) was added dropwise to the mixture via syringe under a nitrogen atmosphere. The reaction temperature was brought to the room temperature, and the mixture was further stirred for 4 h under nitrogen atmosphere. After completion of the reaction, the reaction mixture was acidified with acetic acid, diluted with water, and then extracted with 50 mL of CH_2Cl_2. When the reaction mixture was concentrated under reduced pressure, the residue was dissolved in 50 mL of CH_2Cl_2 and washed twice with water and saturated saline solution. The organic layer was collected, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by column chromatography using hexane/EtOAc (20/80, v/v) to give the desired product as orange-pink crystalline solid (0.29 g, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11 (d, $J =$ 8.4 Hz, 2H), 6.99 (d, $J =$ 8.4 Hz, 2H), 4.15 (q, $J =$ 7.2 Hz, 2H), 4.06 (t, $J =$ 6.0 Hz, 2H), 3.29 (s, 2H), 2.62 (s, 6H), 2.54 (t, $J =$ 6.0, 2H), 2.17−2.13 (m, 2H), 1.50 (s, 6H), 1.26 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.3, 159.9, 158.9, 145.7, 143.5, 131.5, 129.2, 126.4, 115.5, 115.2, 84.2, 76.2, 67.1, 60.7, 30.9, 29.9, 24.8, 14.4, 13.7. IR: 3293, 3257, 2936, 1719, 1529, 1474, 1394, 1368, 1316, 1288, 1272, 1244, 1196, 1178, 1004, 953, 806, 766, 707 cm^{-1}. ESI-MS [M]$^+$ ($C_{29}H_{29}BF_2N_2O_3$) calcd, *m/z* = 502.2; found, *m/z* = 503.1. It shows absorption maximum at 538 nm and emission maximum at 552 nm in CH_2Cl_2 solution.

Polymer A. BODIPY dye **4a** (0.133 mmol, 94 mg), BODIPY dye **6a** (0.139 mmol, 70 mg), and CuI (2 mg) were added to a 100-mL flask under a nitrogen atmosphere. In the glovebox, $Pd(PPh_3)_4$ (5 mg) was added to the flask. When a degassed mixed solution of anhydrous THF (20 mL) and anhydrous diisopropylamine (20 mL) were added to the flask, the mixture was stirred under reflux for 24 h. After removal of the solvent, the residue was dissolved in methylene chloride. The organic layer was washed with water, dried over anhydrous $MgSO_4$, and filtered. Then the filtrate was concentrated under reduced pressure and added to 200 mL of ethanol to precipitate the polymer. The precipitated solid was collected, washed with ethanol, and dried under vacuum for 24 h at room temperature to obtain dark-violet solid (0.102 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11 (d, 2H), 6.99 (d, 2H), 4.15 (broad q, 2H), 4.06 (broad t, 2H), 2.62 (s, 6H), 2.54 (broad t, 2H), 2.17−2.13 (broad m, 2H), 1.42 (s, 6H), 1.27 (broad t, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.3, 159.9, 158.1, 143.3, 142.3, 131.5, 129.2, 126.9, 116.5, 115.5, 89.0, 67.1, 60.7, 30.9, 29.9, 24.8, 14.4, 13.7. IR: 2925, 1732, 1608, 1513, 1472, 1436, 1390, 1313, 1226, 1164, 1088, 836, 765, 703 cm^{-1}. It shows absorption maximum at 659 nm and emission maximum at 678 nm in CH_2Cl_2 solution. GPC (THF, polystyrene standard), M_n = 16 500 g/mol; polydispersity = 1.8.

Compound 1b. When 200 mL of DMF was added to a 500-mL three-neck round-bottom flask containing 3,4-dihydroxybezaldehyde (59.7 mmol, 8 g), ethyl 4-bromobuterate (143.3 mmol, 27.9 g), and K_2CO_3 (238.8 mmol, 32.4 g) under a nitrogen atmosphere, the mixture was stirred for 4 h at 80 °C under a nitrogen atmosphere. After completion of the reaction (which was monitored by TLC), DMF was removed from the mixture under reduced pressure. The residue was dissolved in 150 mL of EtOAc and washed with water and saturated saline solution twice. The organic layer was collected, dried over $MgSO_4$, and concentrated under reduced pressure. The resulting crude product was purified by silica gel column chromatography using hexane/EtOAc (70/30, v/v) to obtain white solid (20.7 g, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.80 (s, 1H), 7.42−7.37 (m, 2H), 6.94 (d, $J =$ 8.0 Hz, 1H), 4.15−4.06 (m, 8H), 2.54−2.49 (m, 4H), 2.17−2.12 (m, 4H), 1.23 (t, $J =$ 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.0, 173.2, 154.4, 149.3, 130.3, 126.9, 112.2, 111.5, 68.1, 68.0, 60.6, 30.8, 30.6, 24.6, 24.5, 14.4.

BODIPY Dye 3b. Compound **1b** (8.72 mmol, 3.19 g) and 2,4-dimethylpyrrole (17.44 mmol, 1.66 g) were added to degassed anhydrous 1000 mL of CH_2Cl_2 in a 2000-mL three-neck round-bottom flask. When eight drops of TFA were added to the reaction mixture, the mixture was stirred in the dark for 12 h at room temperature under nitrogen atmosphere. After the completion of aldehyde (**1b**) (which was conformed by TLC), DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) (8.72 mmol 1.974 g) in CH_2Cl_2 was added. After the mixture was stirred for 30 min, DIEA (diisopropylethylamine) (17 mL) and $BF_3 \cdot OEt_2$ (17 mL) were added. When the mixture was stirred for 1/2 h, it was concentrated to 200 mL and filtered. The filtrate was washed twice with water and brine solution, dried over $MgSO_4$,and concentrated under reduced pressure. The crude product was purified by column chromatography using hexane/EtOAc (90/10 to 70/30, v/v) to obtain a dark brown crystalline solid (1.8 g, 37%). ^1H NMR (400 MHz, $CDCl_3$): δ 6.95 (d, J = 8.4 Hz, 1H), 6.78−6.76 (m, 2H), 5.95 (s, 1H), 4.17−4.05 (m, 6H), 3.98 (t, J = 6.0 Hz, 2H), 2.56−2.48 (m, 10H), 2.18−2.08 (m, 4H), 1.44 (s, 6H), 1.26−1.20 (m, 6H). ^{13}C NMR (100 MHz, CDC_{13}): δ 173.3, 173.2, 155.5, 149.7, 149.6, 143.3, 141.7, 131.8, 127.7, 121.3, 121.1, 114.3, 113.9, 68.5, 68.2, 60.6, 30.8, 24.8, 14.7, 14.6, 14.4. IR: 2926, 1739, 1720, 1543, 1509, 1470, 1413, 1371, 1306, 1265, 1160, 1134, 1060, 1037, 1007, 975, 954, 824, 802, 760, 744, 726 cm^{-1}. ESI-MS $[M + Na]^+$ ($C_{31}H_{39}BF_2N_2O_6Na$) calcd, m/z = 607.3; found, m/z = 607.3. It shows absorption maximum at 502 nm and emission maximum at 511 nm in CH_2Cl_2 solution.

BODIPY Dye 4b. When iodic acid (6.13 mmol, 1.08 g) in 5 mL of water was added dropwise to the ethanol solution (50 mL) containing BODIPY dye **3b** (3.1 mmol 1.8 g) and iodine (6.7 mmol 0.85 g) over 30 min, the mixture was stirred for 2 h. After the completion of the reaction, the reaction mixture was concentrated under reduced pressure and dissolved in CH_2Cl_2. The organic layer was washed twice with water and with saturated saline solution, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by column chromatography using hexane/EtOAc (80/20, v/v) to yield **4b** as red crystals (2.5 g, 98%). ^1H NMR (400 MHz, $CDCl_3$): δ 6.97 (d, J = 8.4 Hz, 1H), 6.75−6.71 (m, 2H), 4.17−4.09 (m, 6H), 3.97 (t, J = 6.0 Hz, 2H), 2.61 (s, 6H), 2.57−2.48 (m, 4H), 2.18−2.08 (m, 4H), 1.45 (s, 6H), 1.27−1.20 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.3, 173.1, 156.8, 150.0, 149.9, 145.5, 141.4, 131.8, 127.2, 120.9, 114.3, 113.6, 85.7, 68.6, 68.2, 60.6, 30.8, 24.8, 17.3, 16.2, 14.4. IR: 2977, 2957, 2772, 2931, 1730, 1539, 1508, 1463, 1396, 1345, 1309, 1265, 1245, 1178, 1138, 1119, 1085, 1048, 989, 956, 758, 724 cm^{-1}. ESI-MS $[M + Na]^+$ ($C_{31}H_{37}BF_2I_2N_2O_6Na$) calcd, m/z = 859.1; found, m/z = 859.4. It shows absorption maximum at 534 nm and emission maximum at 549 nm in CH_2Cl_2 solution.

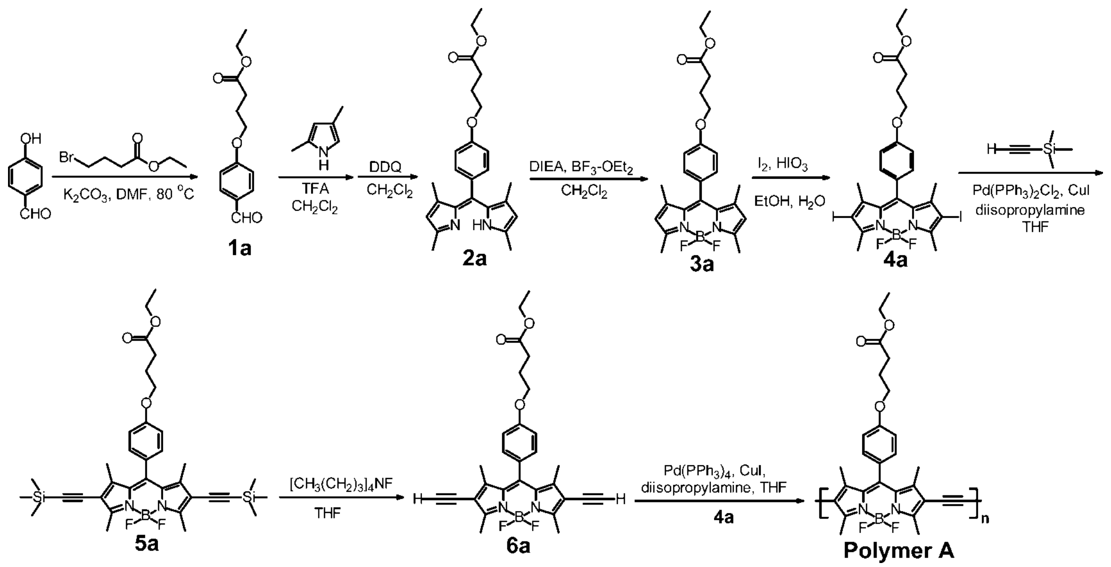
BODIPY Dye 5b. BODIPY dye **4b** (1.7 mmol, 1.5 g), CuI (0.02 mmol, 4 mg) and $Pd(PPh_3)_2Cl_2$ (0.02 mmol, 15 mg) were added to a 100-mL three-neck round-bottom flask under nitrogen atmosphere. When degassed anhydrous THF (20 mL), anhydrous diisopropylamine (20 mL), and trimethylsilylacetylene (5.3 mmol, 0.52 g) were added to the flask, the mixture was stirred under reflux for 4 h. After the completion of the reaction (which was monitored by TLC), the reaction mixture was concentrated under reduced pressure, dissolved in 50 mL of CH_2Cl_2, and washed twice with water and saturated saline solution. The organic layer was collected, dried over $MgSO_4$, and concentrated under reduced pressure. The product was purified by silica gel column chromatography using hexane/EtOAc (95/5 to 70/30, v/v) to yield orange-red solid (1.07 g, 82%). ^1H NMR (400 MHz, $CDCl_3$): δ 6.96 (d, J = 8.4 Hz, 1H), 6.74−6.71 (m, 2H), 4.15−4.07 (m, 6H), 3.97 (t, J = 6.0 Hz, 2H), 2.60 (s, 6H), 2.57−2.48 (m, 4H), 2.18−2.09 (m, 4H), 1.52 (s, 6H), 1.27−1.20 (m, 6H), 0.19 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.3, 173.1, 158.8, 149.9, 149.8, 145.0, 142.7, 131.4, 127.0, 120.9, 116.4, 114.3, 113.6, 101.9, 97.3, 68.6, 68.2, 60.6, 30.8, 24.8, 14.4, 13.7, 13.6, 0.28. IR: 2921, 2852, 2201, 1604, 1513, 1467, 1435, 1389, 1363, 1310,1263, 1227, 1162, 1083, 994, 814, 760, 724 cm^{-1}. ESI-MS $[M]^+$ ($C_{41}H_{55}BF_2N_2O_6Si_2$) calcd, m/z = 776.4; found, m/z = 776.9. It shows absorption maximum at 554 nm and emission maximum at 570 nm in CH_2Cl_2 solution.

BODIPY Dye 6b. When BODIPY dye **5b** (0.65 mmol, 0.50 g) was dissolved in degassed THF (8 mL) in a 50-mL flask at −70 °C, tetrabutylammonium fluoride (TBAF) (2.6 mmol, 2.6 mL of 1 M solution) was added dropwise to the mixture via syringe under nitrogen atmosphere. The reaction temperature was brought to room temperature, and the mixture was further stirred for 4 h under nitrogen atmosphere. After completion of the reaction, the reaction mixture was acidified with acetic acid, diluted with water, and then extracted with 50 mL of CH_2Cl_2. The organic layer was washed twice with water and saturated saline solution. The organic layer was collected, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by column chromatography using hexane/EtOAc (20/80, v/v) to give the product as orange-pink crystalline solid (0.29 g, 75%). ^1H NMR (400 MHz, $CDCl_3$): δ 6.97 (d, J = 8.4 Hz, 1H), 6.76−6.71 (m, 2H), 4.15−4.07 (m, 6H), 3.96 (t, J = 6.0 Hz, 2H), 3.30 (s, 2H), 2.60 (s, 6H), 2.57−2.48 (m, 4H), 2.18−2.09 (m, 4H), 1.54 (s, 6H), 1.27−1.20 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.3, 173.1, 158.9, 150.0, 149.9, 145.7, 143.2, 131.4, 126.8, 120.9, 115.2, 114.3, 113.6, 84.3, 76.1, 68.6, 68.2, 60.6, 30.8, 24.8, 14.4, 13.7, 13.6. IR: 3296, 3255, 2958, 2933, 1728, 1532, 1467, 1392, 1316, 1265, 1247, 1184, 1084, 1013, 995, 761 cm^{-1}. ESI-MS $[M + Na]^+$ ($C_{35}H_{39}BF_2N_2O_6Na$) calcd, m/z = 655.3; found, m/z = 655.9. It shows absorption maximum at 539 nm and emission maximum at 553 nm in CH_2Cl_2 solution.

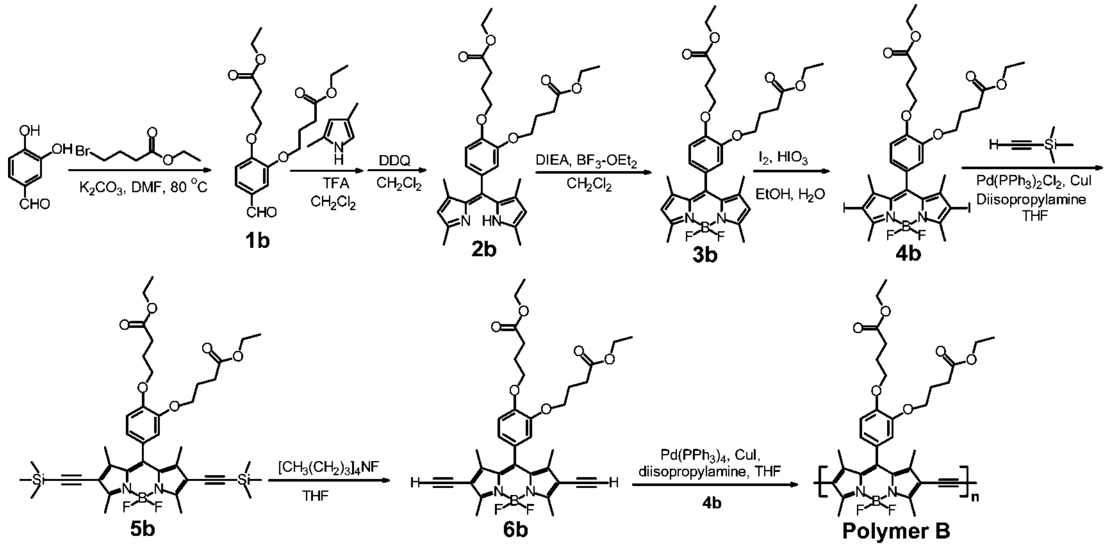
Polymer B. BODIPY dye **4b** (0.81 mmol, 0.677 g), BODIPY dye **6b** (0.84 mmol, 0.531 g), and CuI (0.01 mmol, 4 mg) were added to a 100-mL round-bottom flask. $Pd(PPh_3)_4$ (10 mg) was added to the flask under a nitrogen atmosphere. When a degassed mixed solution of anhydrous THF (20 mL) and anhydrous diisopropylamine (20 mL) were added to the flask, the mixture was stirred under reflux for 24 h. After removal of the solvent, the residue was dissolved in methylene chloride and washed with water. The organic layer was collected, dried over anhydrous $MgSO_4$, and filtered. Then the filtrate was concentrated under reduced pressure and added to 200 mL of ethanol to precipitate the polymer. The precipitated solid was collected, washed with ethanol, and dried under vacuum for 24 h at room temperature to obtain dark-violet solid (0.912 g). ^1H NMR (400 MHz, $CDCl_3$): δ 6.96 (br, 1H), 6.73 (br, 2H), 4.15−4.09 (br, 6H), 3.97 (br, 2H), 2.62 (s, 6H), 2.55−2.49 (br, 4H), 2.14−2.10 (br, 4H), 1.54 (s, 6H), 1.25−1.20 (br, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.3, 173.1, 158.2, 150.0, 149.8, 143.3, 142.3, 131.7, 126.9, 120.9, 116.5, 114.2, 113.6, 89.0, 68.6, 68.2, 60.6, 31.1, 30.8, 24.8, 14.4, 13.8, 13.7. IR: 2932, 1729, 1513, 1471, 1436, 1390, 1311, 1264, 1228, 1161, 1087, 992, 882, 816, 760, 725, 694, 681 cm^{-1}. It displays absorption maximum at 665 nm and emission maximum at 683 nm in CH_2Cl_2 solution. GPC (THF, polystyrene standard), M_n = 23 800 g/mol; polydispersity = 1.9.

9,9-Bis(6′-(hexylthio)hexyl)-2,7-diiodo-9H-fluorene (7a)**.** When 150 mL of degassed DMF was added to a 250-mL three-neck round-bottom flask containing 9,9-bis-(6′-bromohexyl)-2,7-diido-9H-fluorene (2.69 mmol, 2 g), hexanethiol (8.07 mmol, 0.95 g), and K_2CO_3 (10.8 mmol, 1.48 g) under a nitrogen atmosphere, the mixture was stirred for 24 h at 40 °C under a nitrogen atmosphere.[17] After completion of the reaction (which was monitored by TLC), the reaction mixture was concentrated under reduced pressure, added

Scheme 3. Synthetic Route to Deep-Red Polymeric BODIPY Dye (Polymer A)



Scheme 4. Synthetic Route to Deep-Red Polymeric BODIPY Dye (Polymer B)



to water, and extracted with EtOAc. The organic layer was washed twice with water and saturated NaCl solution, dried over anhydrous MgSO$_4$, and concentrated under reduced pressure. The resulting crude product was purified by silica gel column chromatography using hexane/EtOAc to obtain brown liquid (1.47 g, 67%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.65−7.61 (m,4H), 7.38 (d, $J = 7.6$, 2H), 2.44−2.35 (m, 8H), 1.89−1.85 (m, 4H), 1.53−1.47 (m, 4H), 1.4−1.22 (m, 20H), 1.15−1.04 (m, 8H), 1.03−0.84 (m, 6H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 152.5, 140, 136.3, 132.1, 121.7, 93.4, 55.5, 40.2, 32.4, 32.3, 31.7, 31.6, 29.9, 29.8, 29.7, 28.8, 23.8, 22.8, 14.3, 14.2. IR: 2924.9, 2853.4, 1593.4, 1567.8, 1448.0, 1409.4, 1393.4, 1377.0, 1279.1, 1255.6, 1054.0, 1003.3, 879.2, 808.1, 738.3 cm^{-1}. ESI-MS M$^+$ ($C_{37}H_{56}I_2S_2$) calcd, $m/z = 818.8$; found, $m/z = 818.7$.

Polymer C. BODIPY dye **6b** (0.126 mmol, 80 mg), 9,9-bis(6′-(hexylthio)hexyl)-2,7-diiodo-9H-fluorene (**7a**) (0.115 mmol, 94 mg), and CuI (2 mg) were added to a 100-mL flask under a nitrogen atmosphere. In the glovebox, Pd(PPh$_3$)$_4$ (5 mg) was added to the flask. When a degassed mixed solution of anhydrous THF (20 mL) and anhydrous diisopropylamine (20 mL) were added to the flask, the mixture was stirred under reflux for 24 h. After removal of the solvent, the residue was dissolved in methylene chloride (5 mL) and added to 400 mL of ethanol to precipitate the polymer. The precipitated solid was filtered and washed with ethanol and hexane. The obtained solid was dried under vacuum for 24 h at room temperature to obtain dark-violet solid (0.147 g). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.65−7.60 (br, 1H), 7.45−7.36 (m, 2H), 7.03−6.99 (br, 1H), 6.84−6.77 (br, 2H), 4.19−4.12 (br, 6H), 4.12−4.00 (br, 2H), 2.76 (s, 6H), 2.59−2.13 (m, 16H), 1.94 (br, 4H), 1.66 (s, 6H), 1.56−1.47 (br, 4H), 1.36−1.09 (m, 34), 0.86−0.84 (br, 6H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 173.3, 173.2, 158.9, 151.1, 149.9, 144.1, 140.7, 132.3, 131.8, 130.8, 125.5, 121.1, 120.2, 116.4, 114.4, 97.7, 68.7, 68.3, 60.7, 40.5, 32.4, 32.2, 31.6, 30.8, 29.8, 28.8, 24.8, 23.9, 22.7, 22.6, 14.5, 14.0, 13.9. IR: 2925.4, 1731.7, 1521.2, 1391.2, 1313.7, 1269.7, 1245.4, 1078.6, 1002.5, 820.6, 760.4 cm^{-1}. It shows absorption maximum at 606 nm and emission maximum at 641 nm in CH$_2$Cl$_2$ solution. GPC (THF, polystyrene standard), $M_n = 21\,600$ g/mol; polydispersity = 2.1.

Polymer D. BODIPY dye **6b** (0.08 mmol, 50 mg), 1,4-diiodo-2,5-didecyloxybenzene (**7b**) (0.072 mmol, 46 mg), and CuI (2 mg) were added to a 100-mL flask under a nitrogen atmosphere. In the glovebox, Pd(PPh$_3$)$_4$ (5 mg) was added to the flask. When a degassed mixed solution of anhydrous THF (20 mL) and anhydrous diisopropylamine (20 mL) were added to the flask, the mixture was

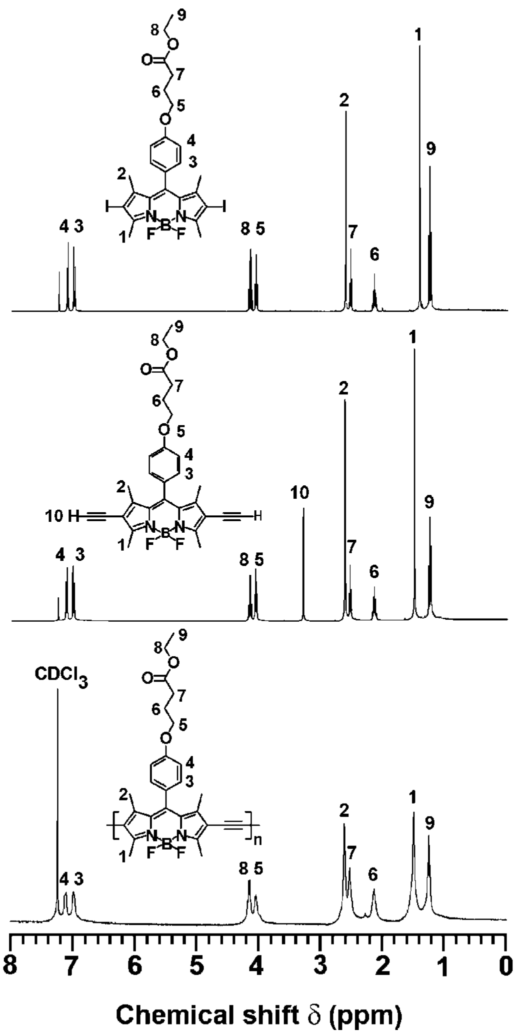


Figure 1. ^{1}H NMR spectra of monomers **4a** and **6a** and polymer **A** in CDCl$_3$ solution.

stirred under reflux for 24 h. The polymer was purified in a way for polymer C to obtain dark-violet solid (0.073 g). ^{1}H NMR (400 MHz, CDCl$_3$): δ 6.99 (br, 1H), 6.85−6.75 (br, 4H), 4.18−4.11 (br, 6H), 3.99−3.92 (br, 6H), 2.72 (s, 6H), 2.58−2.49 (m, 4H), 2.18−2.12 (br, 4H), 1.75 (br, 4H), 1.62 (s, 6H), 1.42 (br, 4H), 1.28−1.20 (br, 30H), 0.86−0.84 (br, 6H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 173.3, 173.1, 158.8, 153.4, 152.0, 149.9, 143.8, 142.3, 131.8, 127.1, 123.4, 121.0, 116.6, 116.0, 114.3, 113.8, 93.5, 87.4, 70.4, 69.5, 68.6, 68.3, 60.7, 33.9, 32.0, 30.9, 29.9, 29.8, 29.7, 29.54, 29.51, 29.4, 26.3, 26.2, 24.8, 22.9, 14.4, 14.4, 14.3, 13.8, 13.7. IR: 2924.6, 1726.2, 1526.4, 1314.8, 1009.7, 762.0 cm^{-1}. It exhibits absorption maximum at 635 nm and emission maximum at 657 nm in CH$_2$Cl$_2$ solution. GPC (THF, polystyrene standard), M_n = 19 200 g/mol; polydispersity = 1.9.

Polymer E. BODIPY dye **6b** (0.126 mmol, 80 mg), 2,5-diiodo-3-decylthiophene (**7c**), (0.115 mmol, 54 mg), and CuI (2 mg) were added to a 100-mL flask under a nitrogen atmosphere. In the glovebox, Pd(PPh$_3$)$_4$ (5 mg) was added to the flask. When a degassed mixed solution of anhydrous THF (20 mL) and anhydrous diisopropylamine (20 mL) were added to the flask, the mixture was stirred under reflux for 24 h. The polymer was purified in a way for polymer **C** to obtain dark-violet solid (0.106 g). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.00−6.98 (m, 2H), 6.76 (br, 2H), 4.18−4.10 (br, 6H), 3.98 (br, 2H), 2.66 (s, 6H), 2.58−2.49 (m, 6H), 2.18−2.12 (br, 4H), 1.57 (br, 8H), 1.27−1.22 (br, 20H), 0.86−0.84 (br, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 173.3, 173.1, 158.7, 150.2, 149.9, 147.4, 144.3, 142.6, 132.7, 131.8, 126.8, 123.1, 121, 116.2, 115.9, 114.3, 113.7, 89.1, 86.4, 76.9, 68.6, 68.2, 60.6, 32.1, 30.8, 30.3, 29.9, 29.8, 29.7, 29.6, 29.5, 24.8, 22.9, 19.9, 14.44, 14.41, 14.3, 13.9, 13.8. IR: 2921.1, 1731.0, 1516.5, 1391.3, 1312.0, 1246.0, 1170.0, 1000.0, 760.0, 724.7 cm^{-1}. It shows absorption maximum at 628 nm and emission maximum at 664 nm in CH$_2$Cl$_2$ solution. GPC (THF, polystyrene standard), M_n = 15 700 g/mol; polydispersity = 2.0.

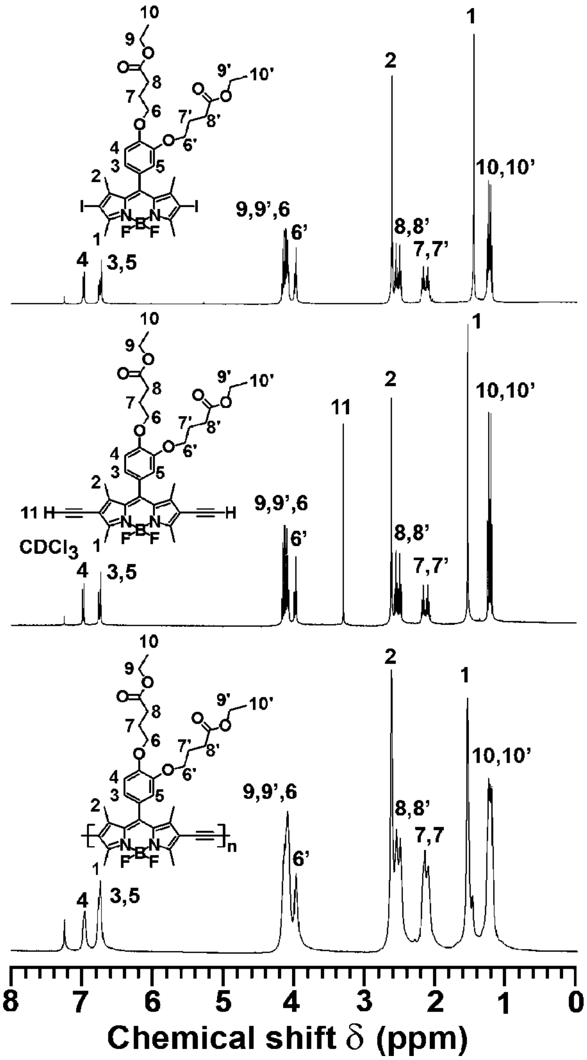
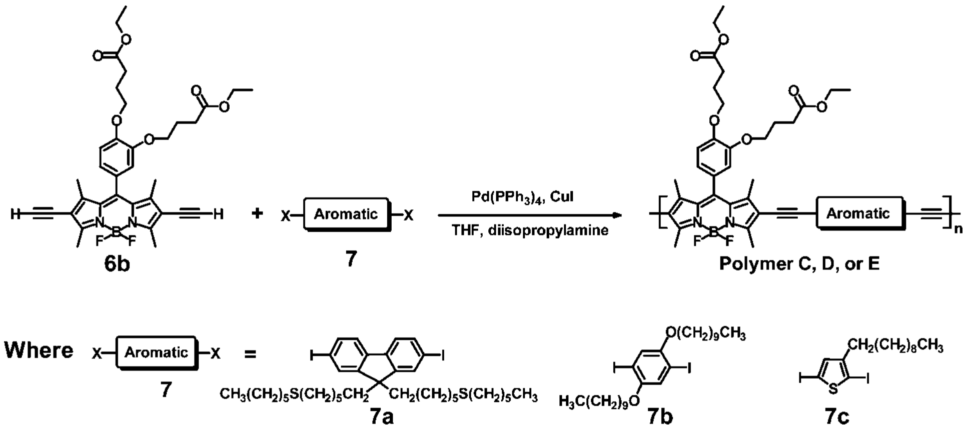


Figure 2. ^{1}H NMR spectra of monomers **4b** and **6b** and polymer **B** in CDCl$_3$ solution.

Results and Discussion

Synthesis and Characterization of the Monomers and Polymers. A variety of aryl groups can be introduced to BODIPY monomers at the meso-position to enhance solubility of BODIPY polymers (Schemes 3 and 4). We employed ethyl phenoxybutanoate side chains instead of phenoxy-*n*-alkyl ones for a future potential use of the ester-functionalized side chains as cell-trappable biosensors. Meso-aryl-substituted BODIPY dyes (**3a** and **3b**) were prepared through the reaction of the formyl benzene derivatives (**1a** and **1b**) with an excess of 2,4-dimethylpyrrole under acid catalysis and followed by oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and treatment with BF$_3$-etherate in the presence of *N*,*N*-diisopropylethylamine (DIEA) (Schemes 3 and 4). Further iodination of BODIPY dyes (**3a** and **3b**) afforded 2,6-diiodo-tetramethyl BODIPY dyes (**4a**

Scheme 5. Synthetic Route to Red Emissive Copolymeric BODIPY Dyes (Polymers C, D, and E)



and **4b**).[14] 2,6-Diethynyl BODIPY monomers (**6a** and **6b**) were prepared by palladium-catalyzed Sonogashira reaction of BODIPY dyes **4a** and **4b** with ethynyltrimethylsilane, affording BODIPY dyes **5a** and **5b**, respectively, and followed by hydrolysis of BODIPY dyes **5a** and **5b** in the presence of tetrabutylammonium fluoride. Diethynylation of BODIPY dye **4a** causes peaks at 1.4 ppm corresponding to the methyl group of BODIPY dye **4a** at position 1 to shift to lower field at 1.5 ppm in BODIPY **6a** and results in an additional peak at 3.3 ppm corresponding to diethynyl groups in BODIPY dye **6a** while other peaks corresponding to positions 2−9 remain unchanged (Figure 1). Conjugated polymers with BODIPY−ethynylene repeated units (**A** and **B**) were synthesized by palladium-catalyzed Sonogashira polymerization of 2,6-diiodo-functionalized BODIPY dyes (**4a** and **4b**) with 2,6-diethynyl-functionalized BODIPY dyes (**6a** and **6b**) (Schemes 3 and 4) in THF solution in the presence of Pd(PPh$_3$)$_4$, CuI, and diisopropylamine.[17,18,21−23] ^{1}H and ^{13}C NMR spectroscopies confirm the molecular structures of polymers in Scheme 2. ^{1}H NMR spectral peaks of polymer **A** become a little broader compared with those of its monomers (**4a** and **6a**) and are almost same as those of monomer **6a**, except the peak corresponding to the monomer diethynyl groups (Figure 1). A similar chemical shift was also observed in the system of polymer **B** (Figure 2). Polymers **A** and **B** exhibit similar solubility to their BODIPY monomers and are soluble in common organic solvents such as chloroform, methylene chloride, and THF.

To further demonstrate the potential tuning of the polymer fluorescence, we incorporated monomers with different band gaps such as fluorene, phenylene, and thiophene units into the polymer backbone of poly(2,6-BODIPY-ethynylene)s (Scheme 5). The BODIPY-based copolymers (polymers **C**, **D**, and **E**) were prepared by palladium-catalyzed Sonogashira polymerization of 2,6-diethynylene-functionalized BODIPY dye monomer **6b** with 9,9-bis(6′-(hexylthio)hexyl)-2,7-diiodo-9H-fluorene (**7a**), 1,4-diiodo-2,5-didecyloxybenzene (**7b**), and 2,5-diiodo-3-decylthiophene (**7c**), respectively (Scheme 5). ^{1}H and ^{13}C NMR spectroscopies confirm the molecular structures of the copolymers in Scheme 2. ^{1}H NMR spectral peaks of polymer **D** become a little broader compared with those of its monomers (**6b** and **7b**). The polymerization of monomer **6b** with monomer **7b** results in the disappearance of the peak at 3.30 ppm corresponding to diethynyl groups in polymer **D** and causes peaks at 2.60 ppm and 1.54 ppm (corresponding to methyl protons of monomer **6b** at positions 2 and 1 to shift to lower field at 2.72 ppm and 1.62 ppm in polymer **D**, respectively (Figure 3). Similar results were also observed in polymer **C** (please see the Supporting Information). The copolymers display similar solubility to that of polymers **A** and **B** and are soluble in common organic solvents such as chloroform, methylene chloride, and THF.

Optical Properties of the Monomers and Polymers. The absorption properties of green emissive BODIPY dye (**3a**) are characterized by a strong $S_0 \rightarrow S_1$ ($\pi-\pi^*$) transition at 501 nm and a weaker broad band around 350 nm ascribed to the $S_0 \rightarrow S_2$ ($\pi-\pi^*$) transition (Figure 4). Introduction of 2,6-diiodo substituents to the BODIPY core leads to large red shifts (33 and 38 nm) of both the UV absorption and fluorescence maxima, respectively, significantly depressing the fluorescence quantum yield because of efficient intersystem crossing induced by the heavy atom effect of iodine (Figure 4, Table 1). 2,6-Diethynylation of 2,6-diiodotetramethyl BODIPY (**4a**) results in a little red shift due to the enhanced conjugation. However, polymer **A** emits in the deep red region at 678 nm and exhibits pronounced bathochromic shifts (158 and 168 nm) of both the absorption and the fluorescence maxima relative to the initial BODIPY dye (**3a**) because of its significant extension of π-conjugation (Figure 5 and Table 1). Polymer **B** displays an absorption maximum at 665 nm and fluorescence maximum at 683 nm, a slight red-shift relative to polymer **A**. The absorption peaks of conjugated polymers become broader than BODIPY monomers as a result of the extended π-conjugation (Figure 4). BODIPY dyes (**3a**, **3b**, **5a**, **5b**, **6a**, and **6b**) show fluorescence lifetimes of several nanoseconds (Table 1). However, the diiodo-functionalized BODIPY dyes (**4a** and **4b**) display much shorter fluorescence lifetimes (ranging from 0.08 to 0.13 ns), consistent with their decreased quantum yields because of efficient intersystem crossing induced by the heavy atom effect of iodine (Table 1).

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(23) Pinto, M. R.; Kristal, B. M.; Schanze, K. S. *Langmuir* **2003**, *19*, 6523.

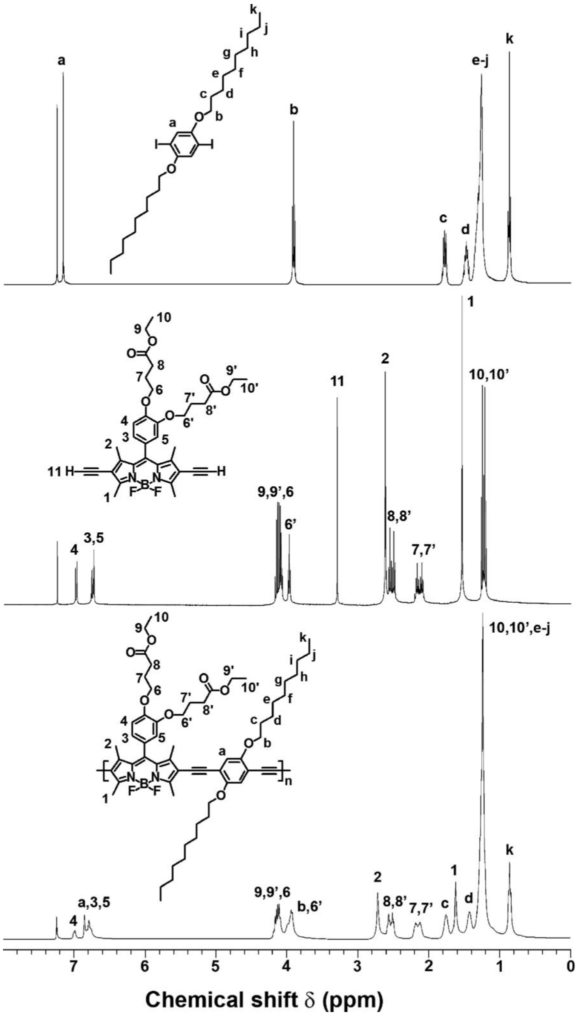

Figure 3. ^{1}H NMR spectra of monomers **7b** and **6b** and polymer **D** in $CDCl_3$ solution.

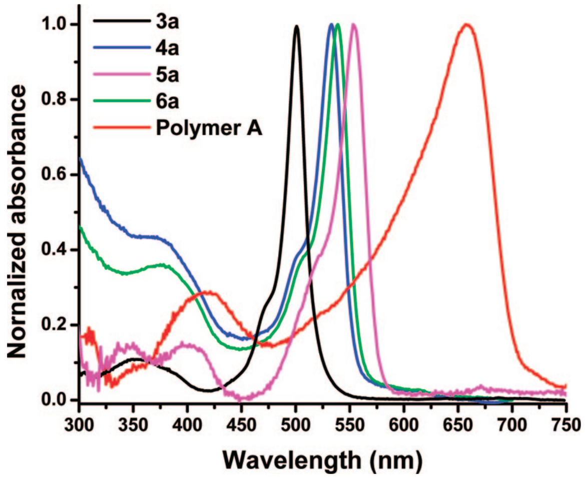

Figure 4. UV−visible absorption spectra of BODIPY dyes and polymer **A** in methylene chloride.

Table 1. Absorption and Emission Maxima and Quantum Yields of BODIPY Dyes and Polymers in Methylene Chloride Solution[a]

	BODIPY dyes or polymers				
	3a	**4a**	**5a**	**6a**	polymer **A**
absorption maxima (nm)	501	533	553	538	659
emission maxima (nm)	510	548	569	552	678
quantum yield (%)	76	5.8	71	63	21
fluorescence lifetime (ns)	3.8	0.13	4.5	4.2	3.8

	BODIPY dyes or polymers				
	3b	**4b**	**5b**	**6b**	polymer **B**
absorption maxima (nm)	502	534	554	539	665
emission maxima (nm)	511	549	570	553	683
quantum yield (%)	81	5.8	79	67	23
fluorescence lifetime (ns)	4.1	0.08	5.2	5.9	3.7

[a] Quantum yields of BODIPY dyes and polymeric dyes were determined by use of fluorescein (quantum yield of 0.85 in 0.1 N NaOH) as a standard.[13−16]

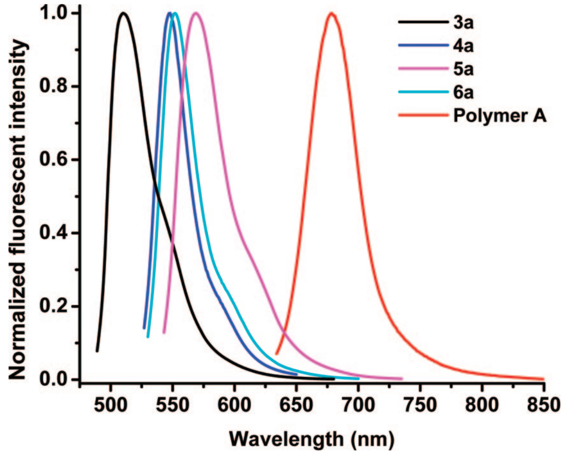

Figure 5. Fluorescence spectra of BODIPY dyes (**3a**, **4a**, **5a**, **6a**) and polymer **A** in methylene chloride. Excitation wavelengths are 485 nm, 520 nm, 521 nm, 530 nm, and 630 nm for BODIPY dyes **3a**, **4a**, **5a**, **6a**, and polymer **A**, respectively.

Arylation at the meso position has no significant effect on the absorption and emission maxima of BODIPY dyes since the arylated moiety is not coplanar with the BODIPY core because of steric hindrance, although the substitution position is structurally different (Table 1).[24] As a result, two different BODIPY monomer pairs (**4a**−**4b** and **6a**−**6b**) each have only 1 nm difference between their respective absorption or emission spectral maxima. However, the absorption and emission maxima of polymer **B** are somewhat more red-shifted relative to those of polymer **A**, which might arise from amplification effect of conjugated polymers. The quantum yields of the meso-phenyl BODIPY dyes (**3b**, **5b**, and **6b**) are a little higher than those of the corresponding less substituted analogues (**3a**, **5a**, and **6a**) (Table 1). The difference might result from reduced free rotation of the phenyl group in the more substituted compounds and a subsequent decrease in loss of energy from the excited states through nonirradiative molecular motions. Polymers **A** and **B** displays similar fluorescence lifetimes to their starting BODIPY dyes (**3a** and **3b**) (Table 1).

As we expected, incorporation of different band gap monomers such as fluorene, benzene, and thiophene units into the backbone of poly(2,6-BODIPY-ethynylene) results in the copolymers with different red emissions. Fluorescence maxima of the copolymers with fluorene, benzene, and thiophene units are 641, 657, and 664 nm, respectively (Table 2 and Supporting Information), which is consistent with their band gap energy

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(24) Sunahara, H.; Urano, Y.; Kojima, H.; Nagano, T. *J. Am. Chem. Soc.* **2007**, *129*, 5597.

Table 2. Absorption and Emission Maxima and Quantum Yields of BODIPY-Based Copolymers in Methylene Chloride Solution[a]

	BODIPY-based copolymers		
	polymer **C**	polymer **D**	polymer **E**
absorption maxima (nm)	606	635	628
emission maxima (nm)	641	657	664
quantum yield (%)	25	24	6
fluorescence lifetime (ns)	2.8	3.6	0.23

[a] Quantum yields of BODIPY dyes and polymeric dyes were determined by use of fluorescein (quantum yield of 0.85 in 0.1 N NaOH) as a standard.[13−16]

differences (fluorene > benzene > thiophene). Introduction of the thiophene unit to poly(2,6-BODIPY-ethynylene) significantly reduces the fluorescence quantum yield of the copolymer and shortens fluorescence lifetime of the copolymer due to efficient intersystem crossing induced by the heavy atom effect of sulfur.[25]

Conclusion

We have successfully synthesized new red and deep-red emissive polymeric BODIPY dyes by exploring 2,6-functionalization of BODIPY dyes. Chemical and photophysical characterizations confirm that BODIPY units were indeed incorporated into the polymer backbones through triple-bond connection between BODIPY cores at positions 2 and 6. Poly(2,6-BODIPY-ethynylene)s display deep-red emission due to significant extension of π-conjugation relative to their parent BODIPY dyes. Incorporation of different band gap monomer units such as fluorene, benzene, and thiophene into poly(2,6-BODIPY-ethynylene)s resulted in the copolymers with different red emissions. A variety of functional groups such as chemical receptors and carbohydrates can be introduced to BODIPY polymers at the meso-position of BODIPY cores for chemical and biological sensing and imaging applications.

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Supporting Information Available: UV−visible absorption and emission spectra of BODIPY dyes and polymers **A**, **B**, **C**, **D** and **E**, comparison of ^{1}H NMR spectra of monomers **6b** and **7a** and polymer **C**, comparison of ^{1}H NMR spectra of monomers **6b** and **7c** and polymer **E**, and ^{1}H and ^{13}C NMR spectra of BODIPY dyes and monomers **7a**−**7c** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(25) de Melo, J. S.; Burrows, H. D.; Svensson, M.; Andersson, M. R.; Monkman, A. P. *J. Chem. Phys.* **2003**, *118*, 1550.