Color Tuning of Polyfluorene Emission with BODIPY Monomers

Ge Meng,[†,‡] Singaravelu Velayudham,[†] Adrian Smith,[†] Rudy Luck,[†] and Haiying Liu*[,†]

Department of Chemistry, Michigan Technological University, 1400 Townsend Drive, Houghton, Michigan 49931, and Department of Pharmacy, School of Medicine, Xi'an Jiaotong University, Xi'an 710061, China

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ABSTRACT: Three fluorescent conjugated copolymers, comprised of alternating fluorene and BODIPY units in the main chain, have been prepared by palladium-catalyzed Suzuki polymerization of 9,9-dihexylfluorene-2,7-diboronic acid with each of three different 2,6-diiodo-substituted BODIPY monomers. The copolymers were characterized using FT-IR spectroscopy, UV−vis spectroscopy, photoluminescence (PL), and molecular weight studies. Low-band gap BODIPY comonomers are effective in expanding the emission wavelength to the orange region because of significant extension of π-conjugation and have significantly enhanced fluorescent intensity with fluorescent quantum yield of up to 85% in methylene chloride solution. The copolymers show absorption maxima between 547 and 557 nm and emission maxima between 585 and 588 nm in methylene chloride solutions. The copolymers possess high molecular weight, good solubility and readily dissolve in common organic solvents such as THF, CH_2Cl_2, $CHCl_3$, and toluene. The copolymers display sensitive fluorescent responses to fluoride and cyanide anions through their multivalent interactions while they do not respond to chloride, bromide, and iodide anions.

Introduction

Polyfluorene and its derivatives have emerged as the most promising light-emitting materials due to their high fluorescence efficiency, excellent chemical and thermal stability, photostability, good solubility and film-forming properties, and the ease with which they can be prepared via high-yielding synthetic routes resulting in well-defined high molar mass polymers.[1−5] Polyfluorene homopolymers possess a large band gap and emit blue light.[5−9] A variety of narrow-band gap monomer units such as 2,1,3-benzoselenadiazole, 2,1,3-naphthoselenadiazole, and 4,7-dithiophen-2′-yl-2,1,3-benzothiazole have been incorporated into the polyfluorene backbone to tune polymer emission wavelengths from orange to red or even to the near-infrared region.[5,10,11]

4-Difluoro-4-bora-3a,4a-diaza-*s*-indacene (BODIPY) derivatives are becoming increasingly popular because BODIPY dyes possess desirable chemical and photostability attributes, relatively high absorption coefficients and fluorescence quantum yields, and contain narrow absorption and emission bands with high peak intensities.[12−14] A variety of strategies to tune optical properties has been achieved by functionalizing BODIPY cores at the meso-, 2,6-, and 3,5-positions, fusing some aromatic rings to the BODIPY core and replacing pyrrole by isoindole.[12−14] However, 2,6-functionalized BODIPY cores have not been fully explored. In addition, BODIPY units have not been reported as part of a conjugated polymer backbone through the 2,6-connection of BODIPY cores where the unique optical properties of BODIPY dyes and fluorene units were combined into one strand of conjugated polymers. In this article, we detail for the first time, the incorporation of three different BODIPY monomers into a polyfluorene backbone through the 2,6-positions of BODIPY cores. This has allowed for the tuning of the polymer emission into the orange region. The syntheses are accomplished by the palladium-catalyzed Suzuki polymerization of 9,9-dihexylfluorene-2,7-diboronic acid with each one of three different 2,6-diiodo-substituted BODIPY monomers, affording polymers **1**, **2**, and **3** (Scheme 1). The absorption and fluorescent maxima of the copolymers in methylene chloride solution are significantly red-shifted (up to 48 and 74 nm) relative to those of the starting BODIPY dyes due to the extended π-conjugation of the conjugated polymers. In addition, these polymers are highly fluorescent with quantum yields ranging from 56% to 85% in methylene chloride solution. The copolymers exhibit no response to chloride, bromide, and iodide anions. However, the presence of fluoride or cyanide anions significantly quenches the fluorescence of the copolymers through their multivalent interactions.

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 $CDCl_3$; 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−vis 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 DMF and calculated by using fluorescein excited at 490 nm in 0.1 N NaOH as the reference quantum efficiency (ϕ_n = 85%).[15−18] Concentration of the copolymers were calculated based on molecular weights of their repeated units. 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 thermostated at 30 °C. 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 measured relative to polystyrene standards. An Enraf Nonius CAD-4 X-ray diffractometer was used in the crystal structure determination. The windows program WinGX was used as the interface for the solution and refinement of the model.[19] The data were first reduced and corrected for absorption using the *psi*-scans and then solved using the program SIR2004.[20] The model was refined using SHELXL97.[21]

* To whom correspondence should be addressed. E-mail: hyliu@mtu.edu.
† Michigan Technological University.
‡ Xi'an Jiaotong University.

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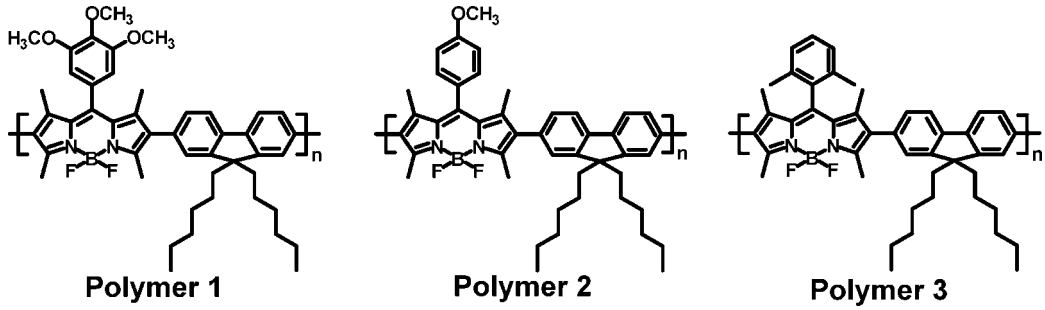
Scheme 1. Chemical Structures of BODIPY-Based Polyfluorene Derivatives



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 standard Schlenk line or drybox techniques under an inert atmosphere of dry nitrogen. Potassium cyanide is highly toxic and should be handled very carefully by wearing gloves and a gas mask.

4,4-Difluoro-8-(3,4,5-trimethoxyphenyl)-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene (3). 3,4,5-Trimethoxylbenzaldehyde (1.65 g, 8.4 mmol) and 2,4-dimethylpyrrole (1.6 g, 16.8 mmol) were dissolved in dry CH_2Cl_2 (800 mL) under a nitrogen atmosphere. Nine drops of trifluoroacetic acid (TFA) (about 0.5 mL) were added, and the mixture was stirred at room temperature overnight. After TLC monitoring showed complete disappearance of the aldehyde, a solution of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (1.9 g, 8.4 mmol) in anhydrous CH_2Cl_2 (200 mL) was added. This mixture was further stirred for 3 h, washed with water three times, dried over anhydrous $NaSO_4$, filtered, and concentrated to dryness. The resulting compound was roughly purified by using aluminum oxide column chromatography to give a brown powder as the crude compound **2** (about 1.0 g, 2.7 mmol, yield of the first step is 32%). This product **2** was used without further purification in the next step. The brown powder (1.0 g, 2.7 mmol) and *N,N*-diisopropylethylamine (DIEA) (16 mL, 168 mmol) were dissolved in anhydrous CH_2Cl_2 (500 mL) under a nitrogen atmosphere. The solution was stirred at room temperature for 30 min, and BF_3-OEt_2 (164 mL, 100 mmol) was subsequently added. This mixture was stirred for 3 h whereupon the complexation was found to be completed by TLC monitoring. The mixture was washed thoroughly with water and brine, dried over anhydrous Na_2SO_4, filtered, and evaporated under vacuum. The crude compound was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate: from first 10:1 to final 5:1, increasing the polarity of the solvent) to give a shiny green powder as the pure BODIPY dye **3** (600 mg, 1.45 mmol, yield of the second step is 53%, yield overall 17%).[22] ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.50 (s, 6H, 2 × CH_3); 2.51 (s, 6H, 2 × CH_3), 3.79 (s, 6H, 2 × OCH_3-3,5), 3.88 (s, 3H, OCH_3-4), 5.97 (s, 2H, Pyr-*H*), 6.49 ppm (d, 2H, Ph-C*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.40 (Py-CH_3), 14.73 (Py-CH_3), 56.57 (OCH_3), 61.50 (OCH_3), 105.40, 121.40, 130.28, 131.52, 138.90, 141.54, 143.24, 154.41, 155.81 ppm. IR (KBr): 3117, 3007, 2954, 2837, 1739, 1578, 1462, 1408, 1384, 1248, 1186 cm^{-1}. MS (EI$^+$): $C_{22}H_{25}BF_2N_2O_3$: *m*/*z* calcd 414.2 (M); found 414 (M$^+$).

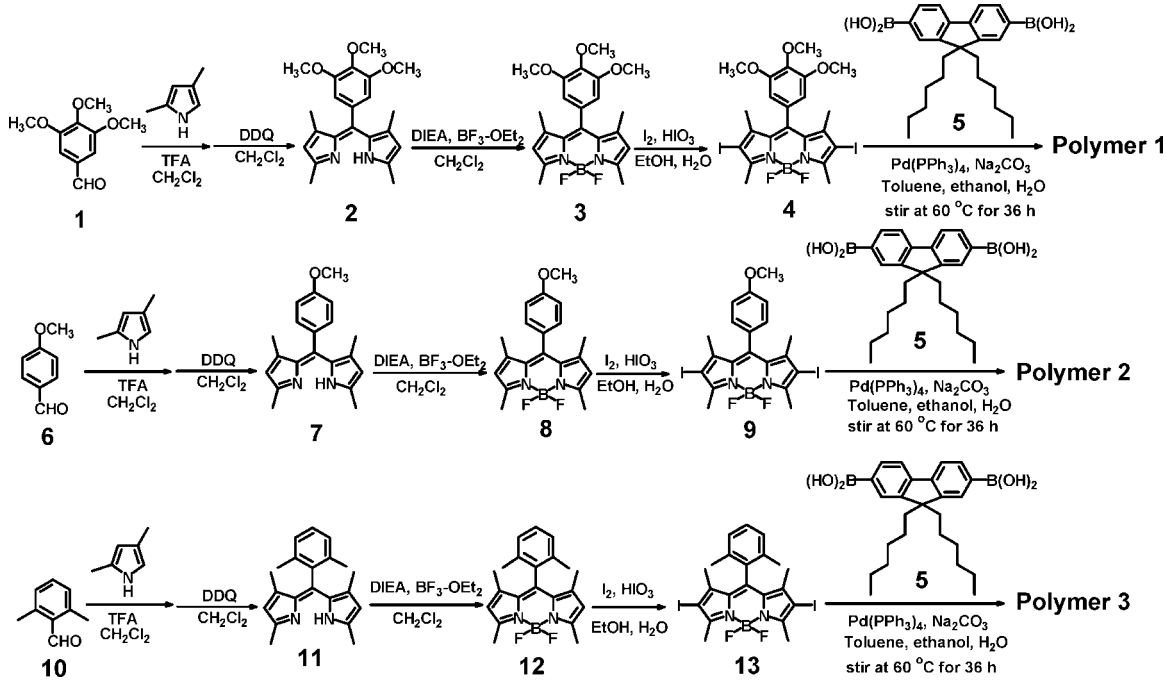
4,4-Difluoro-8-(3,4,5-trimethoxyphenyl)-2,6-diiodo-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene (4). Iodic acid (176 mg, 1 mmol) dissolved in a minimal amount of water was added dropwise over 20 min to a solution of BODIPY dye **3** (207 mg, 0.5 mmol) and iodine (158 mg, 1.25 mmol) in EtOH (40 mL). This mixture was stirred at 60 °C for 30 min. After cooling, the mixture was evaporated under vacuum. The crude product was purified by silica gel column chromatography from ethyl acetate and *n*-hexane to afford a golden compound as pure BODIPY dye **4** (287 mg, 430 mmol, yield 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.55 (s, 6H, 2 × CH_3), 2.64 (s, 6H, 2 × CH_3), 3.83 (s, 6H, 2 × OCH_3-3,5), 3.93(s, 3H, OCH_3-4), 6.48 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.22, 17.09, 56.63, 61.61, 85.40, 105.15, 129.91, 131.43, 139.32, 141.17, 145.47, 154.68, 157.11 ppm. IR (KBr): 2927, 2845, 2279, 1742, 1575, 1525, 1505, 1489, 1464, 1450, 1405, 1384, 1369, 1342, 1324, 1306, 1230, 1165, 1117, 1093, 1075, 1043 cm^{-1}. MS (EI$^+$): $C_{22}H_{23}BF_2I_2N_2O_3$: *m*/*z* calcd 666.0 (M); found 666 (M$^+$).

Polymer 1. To a mixture of BODIPY dye **4** (50 mg, 0.075 mmol, 1 equiv), $Pd(PPh_3)_4$ (tetrakis(triphenylphosphine)palladium) (2.6 mg, 0.005 mmol, 0.6%), and 9,9-dihexylfluorene-2,7-diboronic acid (**5**) (35 mg, 0.083 mmol, 1.1 equiv) was added a degassed mixture of toluene (10 mL), EtOH (4 mL), and H_2O (4 mL) containing Na_2CO_3 (80 mg, 10 equiv) under a nitrogen atmosphere. The mixture was vigorously stirred at 85 °C for 72 h, and then the solvent was evaporated under vacuum. The residue was dissolved in 100 mL of ethyl acetate and washed with water three times. The organic layer was collected, dried over anhydrous Na_2SO_4, and filtered. The filtrate was concentrated and added to ethanol to precipitate the polymer. A red powder was obtained by filtration, further washed with ethanol, and then dried under vacuum for 24 h to afford polymer **1** in a yield of 69%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.72 (t, 6H, 2 × CH_3), 1.04 (m, 16H, 8 × CH_2), 1.52 (s, 6H, 2 × CH_3), 1.95 (br, 2H, 2 × CH_2), 2.58 (br, 6H, 2 × CH_3), 3.86 (br, 6H, 2 × OCH_3), 3.88 (br, 3H, OCH_3), 6.63 (2H, Bodipy-Ph-*H*), 7.15 (4H, Ph-*H*), 7.72 ppm (d, 2H, Ph-*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.87 (1C, Pyr-CH_3), 13.69, 14.13, 22.61, 24.01, 29.75, 31.66, 36.68, 40.58, 55.34, 56.66, 61.53, 105.53, 119.76, 124.91, 129.05, 131.50, 132.46, 134.53, 139.06, 140.02, 141.77, 151.16, 154.59, 154.73, 162.76 ppm. IR (KBr): 2928, 2855, 2051, 1677, 1578, 1456, 1387, 1228, 1176 cm^{-1}. GPC (THF, polystyrene standard), M_n: 22 500 g/mol; polydispersity: 1.75. It displays UV−vis absorption maxima at 557 nm and emission maxima at 587 nm in methylene chloride solution.

4,4-Difluoro-8-(4-methoxyphenyl)-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene (8). BODIPY dye **8** was prepared from 4-methoxybenzaldehyde (**6**) in 28% yield according to the method for BODIPY dye **3**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.43 (s, 6H, 2 × CH_3); 2.55 (s, 6H, 2 × CH_3), 3.87 (s, 3H, 2 × OCH_3-4), 5.97 (s, 2H, Pyr-*H*), 7.01 (d, 2H, Ph-C*H*, J = 8.4), 7.17 ppm (d, 2H, Ph-C*H*, J = 8.4). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.75, 55.50, 114.73, 121.29, 127.26, 129.41, 132.07, 142.07, 143.36, 155.47, 160.35 ppm. IR (KBr): 3038, 2967, 2932, 2841, 1609, 1573, 1538, 1505, 1463, 1441, 1407,1368, 1303, 1289, 1246, 1184, 1155, 1109, 1075, 1050, 1022 cm^{-1}. MS (EI$^+$): $C_{20}H_{21}BF_2N_2O_3$: *m*/*z* calcd 354.2 (M); found 354 (M$^+$).[23]

4,4-Difluoro-8-(4-methoxyphenyl)-2,6-diiodo-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene (9). BODIPY dye **9** was prepared from 4,4-difluoro-8-(4-methoxylphenyl)-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene (**8**) in 88% yield according to the method for BODIPY dye **4**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.43 (s, 6H, 2 × CH_3), 2.62 (s, 6H, 2 × CH_3), 3.87 (s, 3H, OCH_3-4), 7.02 (d, 2H, Ph-*H*, J = 8.4), 7.12 ppm (d, 2H, Ph-*H*, J = 8.4). ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.21, 17.38, 55.61, 85.74, 115.08, 126.89, 129.30, 131.95, 141.80, 145.58, 156.78, 160.77 ppm. IR (KBr): 2953, 2925, 2837, 2041, 1723, 1609, 1572, 1458, 1397, 1345, 1290, 1174, 1117 cm^{-1}. MS (EI$^+$): $C_{20}H_{19}BF_2I_2N_2O_3$: *m*/*z* calcd 605.9 (M); found 606 (M$^+$).

Scheme 2. Synthetic Route to Fluorescent BODIPY-Based Conjugated Copolymers



Polymer 2. Polymer **2** was prepared from BODIPY dye **9** with 9,9-dihexylfluorene-2,7-diboronic acid in 54% yield according to the method for polymer **1**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.67 (d, 6H, 2 × CH_3), 0.95 (m, 16H, 8 × CH_2), 1.67 (s, 6H, 2 × CH_3), 1.88 (4H, 2 × CH_2), 2.16−2.60 (m, 6H, 2 × CH_3), 3.80 (s, 3H, OCH_3), 6.99 (2H, Ph-*H*), 7.07 (4H, Ph-*H*), 7.66 ppm (3H, Bodipy-Ph-*H*). IR (KBr): 2927, 2856, 1724, 1610, 1529, 1458, 1388, 1292, 1176 cm^{-1}. GPC (THF, polystyrene standard), M_n: 19 100 g/mol; polydispersity: 1.65. It displays UV−vis absorption maxima at 547 nm and emission maxima at 585 nm in methylene chloride solution.

4,4-Difluoro-8-(2,6-dimethylphenyl)-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene (12). BODIPY dye **12** was prepared from 2,6-dimethylbenzaldehyde (**10**) in 67% yield according to the method for BODIPY dye **3**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.36 (s, 6H, 2 × CH_3), 2.15 (s, 6H, 2 × CH_3), 2.56 (s, 6H, 2 × CH_3-2,6), 5.97 (s, 2H, Pyr-*H*), 7.13−7.27 ppm (m, 3H, Ph-*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.49 (Py-*C*H_3), 14.86 (Py-*C*H_3), 19.77 (Ph-*C*H_3), 121.08 (Py-C), 128.39, 129.09, 130.55, 134.30, 135.45, 141.40, 142.40, 155.49 ppm. MS (EI$^+$): $C_{21}H_{23}BF_2N_2$: *m*/*z* calcd 352.2 (M); found 352 (M$^+$).[24] IR (KBr): 2962, 2923, 2856, 1541, 1466, 1369, 1258, 1189 cm^{-1}. Single crystals of compound **12** (0.40 × 0.40 × 0.40 mm) were grown by vapor diffusion of hexane into a solution of the compound in ethyl acetate. A suitable crystal was cut to size, rolled in epoxy resin, and mounted on a glass fiber. Crystal data for BODIPY dye **12**: $C_{21}H_{23}BF_2N_2$, monoclinic, space group *C*2/*c*, a = 20.442 (5) Å, b = 7.847(2) Å, c = 25.831(8) Å, β = 112.49 (2)°, V = 3828.4(18) Å^3, Z = 8, D_c = 1.223 g cm^{-1}, μ(Mo Kα) = 0.09 mm^{-1}, T = 293(2) K. Independent reflections measured = 2496, R_1 = 0.059, wR_2 = 0.190 for 2496 independent observed reflections [$F > 4\sigma(F)$], S = 1.04. Full crystallographic details for this structure are available as Supporting Information.

4,4-Difluoro-8-(2,6-dimethylphenyl)-2,6-diiodo-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene (13). BODIPY dye **13** was prepared from 4,4-difluoro-8-(2,6-dimethylphenyl)-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene (**12**) in 90% yield according to the method for BODIPY dye **4**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.23 (s, 6H, 2 × CH_3), 2.12 (s, 6H, 2 × CH_3), 2.65 (s, 6H, 2 × CH_3-2,6), 7.15−7.32 ppm (m, 3H, Ph-*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.93, 16.28, 19.83, 85.63 (Py-C-I), 128.71, 129.70, 130.44, 133.99, 135.32, 141.37, 144.68, 156.82 ppm. IR (KBr): 3063, 3018, 2957, 2916, 2856, 1736, 1596, 1459, 1343, 1241, 1173, 1085 cm^{-1}. MS (EI$^+$): $C_{21}H_{21}BF_2I_2N_2O_3$: *m*/*z* calcd 603.99 (M); found 604 (M$^+$).

Polymer 3. Polymer **3** was prepared from BODIPY dye **13** with 9, 9-dihexylfluorene-2,7-diboronic acid in 52% yield, according to the method for polymer **1**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.66 (m, 6H, 2 × CH_3), 0.98 (m, 12H, 6 × CH_2), 1.30 (t, 6H, 2 × CH_3), 1.58 (broad, 4H, 2 × CH_2), 1.90 (s, broad, 4H, 2 × CH_2), 2.19 (t, 6H, 2 × CH_3), 2.52 (d, 6H, 2 × CH_3), 7.09 (broad, 6H, Ph-*H*), 7.65 ppm (2H, Bodipy-Ph-*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.06 (1C, Pyr-*C*H3), 11.82, 13.75, 14.15, 19.94, 20.11, 22.64, 24.01, 29.76, 31.67, 40.49, 55.35, 119.67, 124.92, 128.47, 129.09, 130.52, 132.51, 134.18, 135.51, 138.21, 139.93, 151.10, 154.36, 215.64 ppm. IR (KBr): 2925, 2855, 1598, 1535, 1457, 1392, 1225, 1176, 1073 cm^{-1}. GPC (THF, polystyrene standard), M_n: 18 400 g/mol; polydispersity: 1.80. It displays UV−vis absorption maxima at 549 nm and emission maxima at 588 nm in methylene chloride solution.

Results and Discussion

Synthesis and Characterization. The synthetic approach to prepare the BODIPY monomers and the polymers is outlined in Scheme 2. Meso-aryl-substituted BODIPY dyes (**3**, **8**, and **12**) were prepared through the condensation of the formyl benzene derivatives (**1**, **6**, and **10**) with 2,4-dimethylpyrrole in the presence of a catalytic amount of TFA and followed by oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and chelation with BF_3-etherate in the presence of *N,N*-diisopropylethylamine (DIEA) (Scheme 2). Further iodization of BODIPY dyes (**3**, **8**, and **12**) afforded 2,6-diiodotetramethyl-BODIPY monomers (**4**, **9**, and **13**). The polymerization reaction was carried out using the well-known palladium-catalyzed Suzuki coupling reaction of 9,9-dihexylfluorene-2,7-diboronic acid with 2,6-diiodo-substituted BODIPY monomers (**4**, **9**, and **13**) in a mixed solution of toluene, ethanol, and water and afforded dark red solids of above polymers in yields of over 52%. All of these polymers readily dissolve in common organic solvents such as THF, CH_2Cl_2, $CHCl_3$, and toluene. ^{1}H and ^{13}C NMR spectroscopies confirm the molecular structures in Schemes 1 and 2. Figure 1 shows the ^{1}H NMR spectra of 9,9-dihexylfluorene-2,7-diboronic acid, monomer **4**, and polymer **1**. Polymerization causes the single peak at 3.93 ppm due to methyl group of monomer **4** at the d position to shift to lower field and overlap at 3.86 ppm with the methyl group at the e

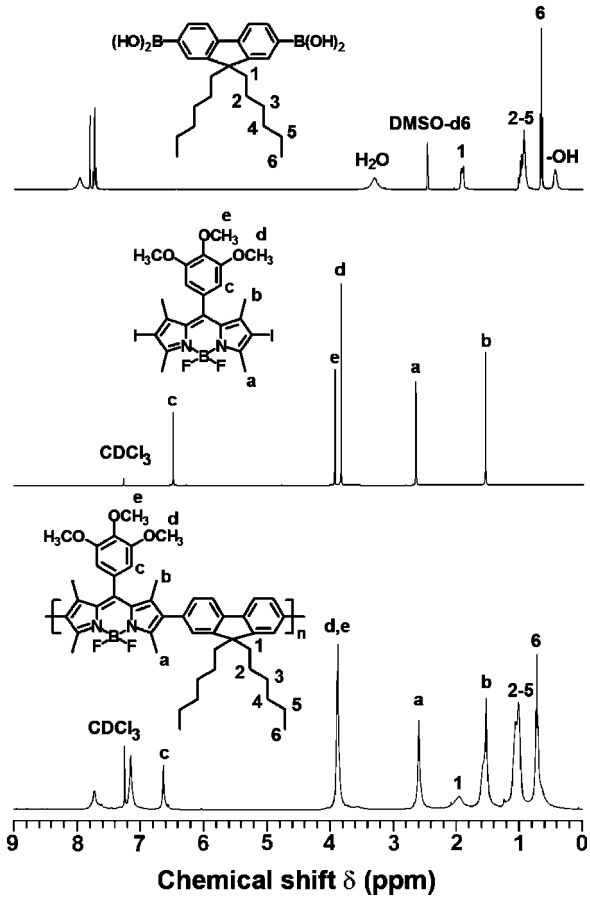


Figure 1. ^{1}H NMR spectra of 9,9-dihexylfluorene-2,7-diboronic acid in DSMO-d_6, monomer **4**, and polymer **1** in $CDCl_3$ solution.

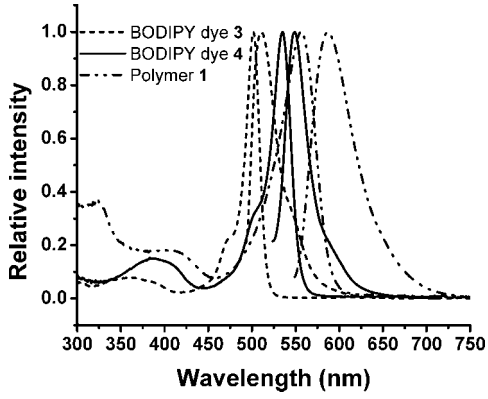


Figure 2. Normalized UV−vis absorption and fluorescent spectra of BODIPY dyes **3** and **4** and polymer **1** in methylene chloride solution.

position (Figure 1). As expected, the ^{1}H NMR signals of the polymers become broader than those of their monomers (Figure 1), due in part to their longer rotational correlation times.

Photophysical Properties. The photophysical characteristics of BODIPY dyes, monomers, and polymers were investigated in methylene chloride and DMF solutions. The absorption properties of the BODIPY dye **3** in methylene chloride solution are characterized by a strong $S_0 \rightarrow S_1$ ($\pi-\pi^*$) transition at 502 nm and a weaker broad band at a shorter wavelength around 356 nm ascribed to the $S_0 \rightarrow S_2$ ($\pi-\pi^*$) transition[12] (Figure 2). BODIPY dyes **8** and **12** display similar absorption features as BODIPY dye **3**. The introduction of the two iodo substituents to the dipyrromethene core (**3**, **8**, and **12**) results in a significant red shift (up to 33 and 38 nm) in the UV absorption and

Table 1. UV−vis Absorption and Emission Spectral Maxima and Fluorescent Quantum Yields of BODIPY Derivatives and Copolymers in CH_2Cl_2 and DMF Solutions

BODIPY	solvent	absorption maxima (nm)	emission maxima (nm)	quantum yield (%)
3	CH_2Cl_2	502	511	72
3	DMF	501	511	55
4	CH_2Cl_2	535	549	7.5
4	DMF	534	551	3.4
polymer **1**	CH_2Cl_2	557	587	64
polymer **1**	DMF	564	590	16
8	CH_2Cl_2	500	510	80
8	DMF	500	510	72
9	CH_2Cl_2	533	548	5.7
9	DMF	533	551	4.9
polymer **2**	CH_2Cl_2	547	585	56
polymer **2**	DMF	554	589	16
12	CH_2Cl_2	501	510	87
12	DMF	502	510	74
13	CH_2Cl_2	535	549	8.6
13	DMF	536	552	4.4
polymer **3**	CH_2Cl_2	549	588	85
polymer **3**	DMF	558	590	16

fluorescent maxima respectively, and significantly quenches the fluorescence quantum yield because of the heavy atom effect (Figures 2−4 and Table 1). Absorption and fluorescence spectra of 2,6-diiodo-substituted BODIPY monomers (**4**, **9**, and **13**) exhibit good mirror symmetry with similar band shapes for the absorption and emission spectra as verified by measuring their full width at half-maximum (Figure 2). When low-band-gap BODIPY units are incorporated into the polyfluorene backbone, the fluorescence corresponding to the fluorene segment completely disappears while the emission consists exclusively of one peak at longer wavelength responsible for the BODIPY units. The complete disappearance of the fluorene segment arises from an efficient photoinduced energy transfer from the fluorene segment to the BODIPY unit which functions as a powerful trap in the copolymer backbone. Extended π-conjugation of the polymer **1** results in significant red shifts (55 and 76 nm) of both the UV−vis absorption and fluorescence maxima, respectively, compared to its starting BODIPY dye (**3**). Similar red shifts were also observed in polymers **2** and **3** (Table 1). In addition, fluorescent conjugated copolymers display slightly broader absorption and emission peaks due to extension of π-conjugation compared to their BODIPY monomers (Figure 2).

BODIPY dyes with different arylated moieties at the meso position (**3**, **8**, and **12**) only display a 1−2 nm difference between their UV−vis absorption spectral maxima or emission spectral maxima although the substitution position is structurally unique (Table 1).[25] Iodization of BODIPY dyes (**3**, **8**, and **12**) at the 2- and 6-positions does not increase this minor difference (Table 1). This minor difference arises from the fact that the arylated moiety is not coplanar with the BODIPY core due to steric hindrance (Figure 3). As a result, arylation at the meso position does not significantly affect the absorption and emission spectral maxima of BODIPY dyes. The extended π-conjugation of polymers **1**, **2**, and **3** also fails to amplify the minor difference of emission spectral maxima of their monomers. However, BODIPY dyes (**3**, **8**, and **12**) possess different fluorescence quantum yields (**12**) (Table 1). BODIPY dye **12** is highly fluorescent with a fluorescence quantum yield of 86.7%. This is the highest among the three BODIPY dyes (**3**, **8**, and **12**). The ortho-methyl groups on the meso-phenyl ring in **12** introduce steric constraints on the phenyl ring and suppress nonradiative deactivation to increase the quantum yield by restricting internal free rotation of the phenyl ring at the meso position relative to the BODIPY core in the excited state (Figure 3). As a result, polymer **3** is highly fluorescent with a

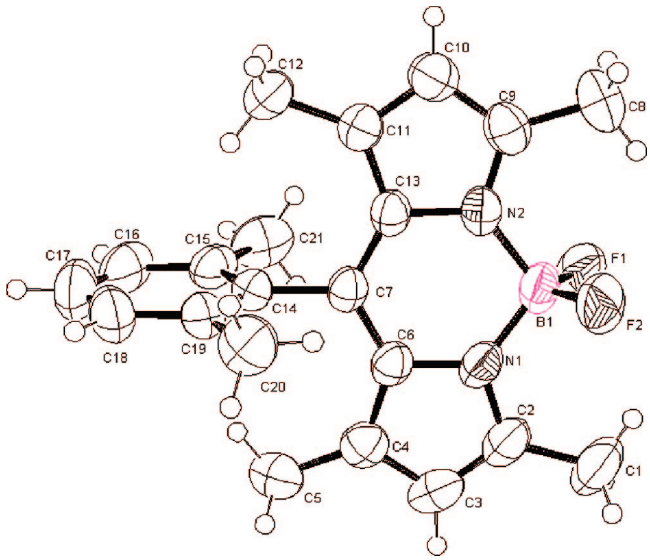


Figure 3. ORTEP representation of the molecular structure of BODIPY dye **12**. The non-H atoms are represented by thermal ellipsoids displayed at the 50% probability level, and the H atoms are indicated by circles of arbitrary radii.

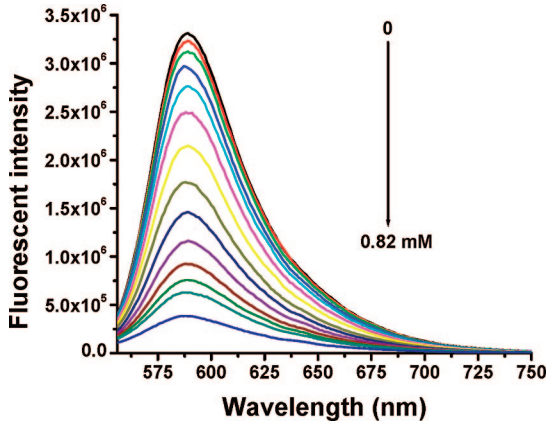


Figure 4. Fluorescence spectra of polymer **1** (3.5 mL, 2.0×10^{-6} M, DMF) in titration with incremental amounts of fluoride anions by addition of a solution of TBAF (tetrabutylammonium fluoride) in DMF (0.05 M). Concentrations of TBAF in the mixed solution from top to bottom curve are 0, 0.064, 0.13, 0.19, 0.26, 0.32, 0.39, 0.45, 0.51, 0.57, 0.63, 0.70, 0.75, and 0.82 mM, respectively. Emission data were collected after 3 min of equilibration at 25 °C.

fluorescence quantum yield of 85% in methylene chloride solution, which is higher than those of polymers **1** and **2**.

The UV−vis absorption and emission maxima of BODIPY dyes (**3**, **4**, **8**, **9**, **12**, and **13**) are relatively insensitive to the solvent polarity with similar shapes of the UV−vis absorption and emission spectra in methylene chloride and DMF (Table 1). The emission maxima of 2,6-diiodo-substituted BODIPY dyes (**4**, **9**, and **13**) undergo bathochromically red shifts by 1−2 nm in a more polar solvent (such as DMF) (Table 1). However, the fluorescent quantum yields of all BODIPY dyes (**3**, **4**, **8**, **9**, **12**, and **13**) decrease in a more polar solvent (DMF) (Table 1). The UV−vis absorption and emission maxima of conjugated copolymers **1**, **2**, and **3** are also slightly red-shifted, and their fluorescent quantum yields decrease significantly in a more polar solvent (DMF) (Table 1).

Polymers **1**−**3** were evaluated for potential responses to anions. The presence of 6 mM tetrabutylammonium salts of anions such as Cl^-, Br^-, and I^- in DMF solutions of polymer **1**, **2**, or **3** or BODIPY dye **3**, **8**, or **12** does not affect the optical spectra of the polymers or the BODIPY dyes. However, titration

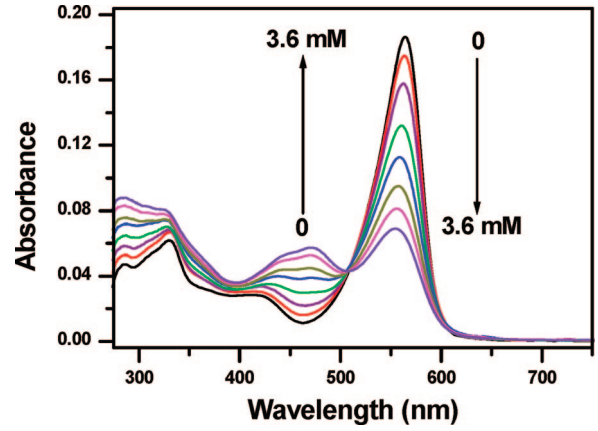


Figure 5. UV−vis absorption spectra of polymer **1** (3.5 mL, 3.0×10^{-5} M, DMF) in titration with incremental amounts of fluoride anions by addition of a solution of TBAF in DMF (0.1 M). Concentrations of TBAF in the mixed solution from top to bottom curve (corresponding to absorption spectral maximum peak at 564 nm) are 0, 0.26, 0.51, 0.76, 1.0, 1.3, 2.4, and 3.6 mM, respectively. Absorption data were collected after 3 min of equilibration at 25 °C.

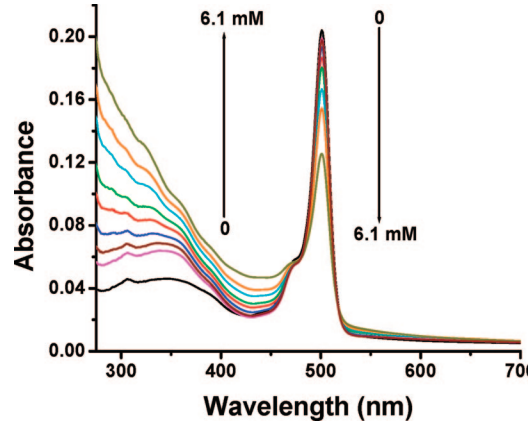


Figure 6. UV−vis absorption spectra of BODIPY dye **3** (3.5 mL, 3.0×10^{-5} M, DMF) in titration with incremental amounts of fluoride anions by addition of a solution of TBAF in DMF (0.1 M). Concentrations of TBAF in the mixed solution from top to bottom curve (corresponding to absorption peak at 501 nm) are 0, 0.26, 0.51, 0.76, 1.9, 2.4, 3.6, 5.3, and 6.1 mM, respectively. Absorption data were collected after 3 min of equilibration at 25 °C.

of tetrabutylammonium fluoride to DMF solution of polymer **1** causes significant quenching of the polymer fluorescence, and a considerable decrease of the maximum absorption spectral peak at 564 nm corresponding to a strong $S_0 \rightarrow S_1$ ($\pi-\pi^*$) transition, and results in the appearance of a new absorption broad band around 465 nm. In addition, the presence of fluoride anions triggered significant blue shifts in the absorption peak at 564 nm. Similar results were also observed in polymers **2** and **3** in the presence of fluoride anions in DMF solution (Supporting Information). The presence of fluoride anions also resulted in fluorescence quenching of BOIDPY dye **3** and a decrease of the absorption peak at 501 nm (Figure 6). However, polymer **1** displays much stronger affinity for fluoride anions than BODIPY dye **3** because of its multivalent interactions with fluoride anions. The changes in the UV−vis and fluorescence spectra of polymers and their corresponding BODIPY dyes may result from decomposition of BODIPY moieties in the presence of fluoride anions as it was reported that fluoride anions cause decomposition of BODIPY dyes.[26] The decomposition of the BODIPY cores in the presence fluoride anions might arise from a nucleophilic displacement which breaks a B−N bond resulting in a B−F bond.[27]

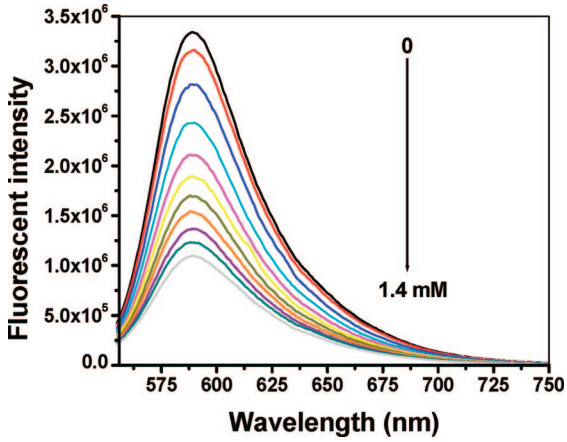


Figure 7. Fluorescence spectra of polymer **1** (3.5 mL, 2.0×10^{-6} M, DMF) in titration with incremental amounts of cyanide anions by addition of a solution of KCN (0.05 M) in of DMF solution with 10% H_2O. Concentrations of KCN in the mixed solution from top to bottom curve are 0, 0.26, 0.38, 0.51, 0.63, 0.76, 0.88, 1.0, 1.1, 1.3, and 1.4 mM, respectively. Emission data were collected after 3 min of equilibration at 25 °C.

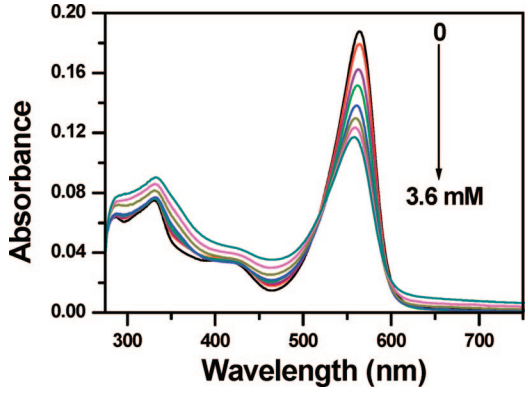


Figure 8. UV−vis absorption spectra of polymer **1** (3.5 mL, 3.0×10^{-5} M, DMF) in titration with incremental amounts of a solution of KCN (0.08 M) in of DMF solution with 10% H_2O. Concentrations of KCN in the mixed solution from top to bottom curve (corresponding to the absorption spectral maximum peak at 564 nm) are 0, 0.26, 0.51, 0.76, 1.3, 2.4, and 3.6 mM, respectively. Absorption data were collected after 3 min of equilibration at 25 °C.

Titration of KCN to DMF solution of polymer **1** also resulted in significant quenching of the polymer fluorescence and considerable decrease of the absorption peak at 564 nm (Figures 7 and 8). However, the fact that a new absorption broad band around 465 nm in the presence of cyanide anions does not appear (Figure 8) while the presence of fluoride anions in DMF solution of polymer **1** results in a new absorption peak around 465 nm, indicates that cyanide anions interact with BODIPY cores differently compared to fluoride anions. Titration of cyanide anions to DMF solution of BODIPY dye **3** caused moderate quenching result in a decrease of the absorption spectral maximum peak at 501 nm corresponding to a strong $S_0 \rightarrow S_1$ ($\pi-\pi^*$) transition, and an increase in a weak absorption shoulder peak at 350 nm corresponding to a $S_0 \rightarrow S_2$ ($\pi-\pi^*$) transition[12] (Figure 9 and Supporting Information). Polymer **1** exhibits much more sensitive fluorescent responses to cyanide anions than its corresponding BODIPY dye due to its multivalent interactions with cyanide anions. Similar results were also observed in polymers **2** and **3** compared to their corresponding BODIPY dyes **8** and **12** (Supporting Information). However, polymer **1** shows a higher affinity for cyanide anions than polymers **2** and **3** (Supporting Information). These results are interesting in light of the related stability of the BODIPY dye

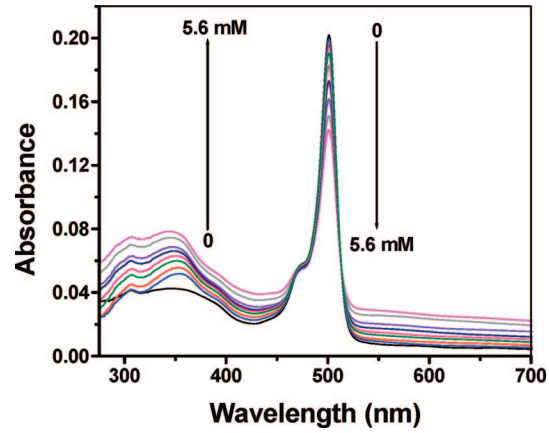


Figure 9. UV−vis absorption spectra of BODIPY dye **3** (3.5 mL, 3.0×10^{-5} M, DMF) in titration with incremental amounts of a solution of KCN (0.08 M) in of DMF solution with 10% H_2O. Concentrations of KCN in the mixed solution from top to bottom curve (corresponding to the absorption spectral maximum peak at 501 nm) are 0, 0.32, 0.63, 1.3, 1.9, 2.4, 3.6, 4.6, and 5.6 mM, respectively. Absorption data were collected after 3 min of equilibration at 25 °C.

in the presence of cyanide anions.[26] Mechanistic details of the fluorescence quenching of the copolymers and their corresponding BODIPY dyes by cyanide anions certainly require further study for potential application in quantitative analysis.

Conclusion

In summary, three light-emitting conjugated copolymers with alternating 9,9′-dihexylfluorene and BODIPY units were synthesized by palladium-catalyzed Suzuki polycondensation. Chemical and photophysical characterizations confirm that BODIPY moieties were indeed incorporated into the polymer backbones. The incorporation of BODIPY monomers into the polyfluorene main chain causes significant red shifts in their UV−vis absorption and emission spectral maxima due to extended π-conjugation of the copolymers relative to their starting BODIPY dyes (**3**, **8**, and **12**). The BOIDPY-based copolymers exhibit sensitive responses to fluoride and cyanide anions, resulting in significant quenching of the polymer fluorescence due to their multivalent interactions with fluoride and cyanide anions while they displayed no responses to chloride, bromide, and iodide anions. Other detailed examples of well-reported alkylation or arylation at the meso position in BODIPY cores will allow for the preparation of a variety of BODIPY-based conjugated copolymers bearing different functional groups such as chemical receptors and carbohydrate residues for chemical and biological sensing applications.

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Supporting Information Available: ^1H and ^{13}C NMR spectra of intermediates and monomers, normalized UV−vis absorption and fluorescent spectra of BODIPY dyes **3**, **4**, **8**, **9**, **12**, and **13** and polymers **1**, **2**, and **3** in methylene chloride and DMF solution, and UV−vis absorption and fluorescent spectra of polymers **1**, **2**, and **3** and BODIPY dyes **3**, **8**, and **12** in the absence and presence of fluoride and cyanide anions; crystallographic data for BODIPY dye

12 in the form of a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Bunz, U. H. F. *Chem. Rev.* **2000**, *100*, 1605–1644.
(2) Thomas, S. W.; Joly, G. D.; Swager, T. M. *Chem. Rev.* **2007**, *107*, 1339–1386.
(3) McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2537–2574.
(4) Liu, B.; Bazan, G. C. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 589–593.
(5) Liu, B.; Bazan, G. C. *Chem. Mater.* **2004**, *16*, 4467–4476.
(6) Xue, C. H.; Donuru, V. R. R.; Liu, H. Y. *Macromolecules* **2006**, *39*, 5747–5752.
(7) Scherf, U.; List, E. J. W. *Adv. Mater.* **2002**, *14*, 477–487.
(8) Knaapila, M.; Winokur, M. J. *Polyfluorenes* **2008**, *212*, 227–272.
(9) Chen, P.; Yang, G. Z.; Liu, T. X.; Li, T. C.; Wang, M.; Huang, W. *Polym. Int.* **2006**, *55*, 473–490.
(10) Chen, S. A.; Lu, H. H.; Huang, C. W. *Polyfluorenes* **2008**, *212*, 49–84.
(11) Tang, C.; Liu, F.; Xu, H.; Huang, W. *Prog. Chem. (Beijing, China)* **2007**, *19*, 1553–1561.
(12) Loudet, A.; Burgess, K. *Chem. Rev.* **2007**, *107*, 4891–4932.
(13) Ulrich, G.; Ziessel, R.; Harriman, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 1184–1201.
(14) Ziessel, R.; Ulrich, G.; Harriman, A. *New J. Chem.* **2007**, *31*, 496–501.
(15) Parker, C. A.; Rees, W. T. *Analyst* **1960**, *85*, 587–600.
(16) Yogo, T.; Urano, Y.; Ishitsuka, Y.; Maniwa, F.; Nagano, T. *J. Am. Chem. Soc.* **2005**, *127*, 12162–12163.
(17) Maruyama, S.; Kikuchi, K.; Hirano, T.; Urano, Y.; Nagano, T. *J. Am. Chem. Soc.* **2002**, *124*, 10650–10651.
(18) Gabe, Y.; Urano, Y.; Kikuchi, K.; Kojima, H.; Nagano, T. *J. Am. Chem. Soc.* **2004**, *126*, 3357–3367.
(19) Farrugia, L. J.; Watson, I. M. *Acta Crystallogr., Sect. C* **1999**, *55*, 326–328.
(20) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr.* **1968**, *A24*, 351–359.
(21) Sheldrick, G. M. SHELX-97. Programs for Crystal Structure Analysis University of Göttingen, Germany, **1998**.
(22) Benniston, A. C.; Copley, G.; Elliott, K. J.; Harrington, R. W.; Clegg, W. *Eur. J. Org. Chem.* **2008**, 2705–2713.
(23) Baruah, M.; Qin, W. W.; Flors, C.; Hofkens, J.; Vallee, R. A. L.; Beljonne, D.; Van der Auweraer, M.; De Borggraeve, W. M.; Boens, N. *J. Phys. Chem. A* **2006**, *110*, 5998–6009.
(24) Yogo, T.; Urano, Y.; Mizushima, A.; Sunahara, H.; Inoue, T.; Hirose, K.; Iino, M.; Kikuchi, K.; Nagano, T. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 28–32.
(25) Sunahara, H.; Urano, Y.; Kojima, H.; Nagano, T. *J. Am. Chem. Soc.* **2007**, *129*, 5597–5604.
(26) Huh, J. O.; Do, Y.; Lee, M. H. *Organometallics* **2008**, *27*, 1022–1025.
(27) Coskun, A.; Akkaya, E. U. *Tetrahedron Lett.* **2004**, *45*, 4947–4949.

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