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Near-infrared emissive BODIPY polymeric and copolymeric dyes

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ABSTRACT

Novel near-Infrared emissive BODIPY polymeric dyes (polymers **A** and **B**) were prepared by Sonogashira cross-coupling reaction of 2,6-diiodo BODIPY dyes bearing one and two styryl groups at 3,5 positions (**5**, **6**) with 2,6-diethynyl BODIPY dye, respectively. These polymeric dyes (**A** and **B**) display absorption maxima at 697 and 738 nm, and emission maxima at 715 and 760 nm, respectively. These polymeric dyes exhibit significant red shifts in absorption and emission maxima due to their extended π -conjugation systems compared with their BODIPY monomeric dyes. The thin films of polymers **A** and **B** display further red shift with emission maxima 764 and 810 nm, respectively. Near-infrared BODIPY copolymeric dye (**C**) was prepared by Sonogashira polymerization of 2,6-diiodo BODIPY dye bearing two styryl groups with 2,5-diethynyl-3-decylthiophene. For comparison in optical properties, deep-red and red emissive BODIPY copolymeric dyes (**D** and **E**) were prepared by Sonogashira polymerization of 2,6-diiodo BODIPY dye bearing monostyryl group and 2,6-diiodo BODIPY dye with 2,5-diethynyl-3-decylthiothene, respectively. These polymers display their absorption maxima at 649 nm and 634 nm, and emission maxima at 694 nm and 669 nm, respectively. All the polymers displayed good thermal stability and solubility in dichloromethane, and their lifetimes ranged from 0.7 to 3.4 ns.

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1. Introduction

BODIPY (4,4'-difluoro-4-bora-3a,4a-diaza-s-indacene) dyes have been well studied because of many distinctive and desirable properties such as high absorption coefficients, narrow absorption and emission bands, sharp emissions, high fluorescence quantum yields, and excellent chemical and photostabilities [1-3]. They have promising applications in supramolecular fluorescent gels [4], solar cells [5], sensing [6-8] and imaging [9]. The extended conjugation of BODIPY units with aromatic, ethynyl, aryl substituents leads to significant red shifts [1-3]. Recently, some near-infrared emissive BODIPY dyes have been prepared for emerging and more challenging biotechnology and biomedical applications [1–3]. Very recently, a few BODIPY-based conjugated oligomers, polymers and copolymers have been reported that combine the unique properties of both BODIPY dyes and conjugated polymers into one package for a variety of potential applications in electronic and biotechnology industry [10-13]. However, most BODIPY-based conjugated oligomers, polymers and copolymers emit from yellow to deep-red emission with wavelength ranges from 580 nm to 698 nm [10–15]. Only one paper has reported BODIPY-based copolymers with near-infrared emission

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from 691 to 720 nm by palladium-catalyzed Sonogashira polymerization of 1,4-diethynyl-2,5-dihexadecyloxybenzene with diiodophenyl-fused BODIPY monomers [15].

Our hypothesis is that significant extension of π -conjugation of BODIPY core with one, two styryl groups at 3,5 positions will help tune BODIPY polymeric dyes to the near-infrared region. In this article, we report near-infrared emissive BODIPY polymeric and copolymeric dyes with emission wavelength range from 715 nm to 760 nm. These polymers were synthesized by palladium-catalyzed Sonogashira coupling reaction of 2,6-diiodo BODIPY derivatives (5,6) with 2,6-diethynyl BODIPY dye (7) (Scheme 1). For comparison of optical properties, deep-red and red emissive BODIPY copolymeric dyes were prepared by palladium-catalyzed Sonogashira of 2,6-diiodo BODIPY dye bearing one styryl group (5) with 2,5-diethynyl-3-decylthiophene (9) and 2,6-diethynyl BODIPY derivative (7) with 2,5-diiodo-3-decylthiophene (8) respectively. Tridodecyloxy groups were introduced to BODIPY monomer (7) at the meso-position to enhance solubility of BODIPY polymers in organic solvents while ethyl esters were introduced to BODIPY monomers at 3,5 positions in order to facilitate easy separation of BODIPY monomers bearing one or two styryl groups (5, 6) and provide a future potential use of the ester-functionalized side chains as cell-trappable biosensors [12]. These BODIPY polymeric and copolymeric dyes have been characterized for optical and thermal properties.





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Scheme 1. Chemical structures of near-infrared, deep-red, red emissive BODIPY polymeric and copolymeric dyes.

2. Experimental

2.1. Instrumentation

¹H NMR and ¹³C NMR spectra were collected on a 400 MHz Varian Unity Inova spectrophotometer instrument. ¹H and ¹³C NMR spectra were recorded in CDCl₃, and chemical shifts (δ) are given in ppm relative to solvent peaks (at 7.24 ppm for ¹H spectra and at 77.3 for ¹³C spectra) 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 0.22 m steady-state fluorometer. Fluorescence quantum yields of BODIPY dyes and polymeric dyes were measured in methylene chloride and calculated by using fluorescein excited at 490 nm in 0.1 N NaOH as the reference (quantum efficiency 85%) [16-19]. Fluorescence lifetimes were measured on a GL-3300 Nitrogen Laser laserstrobe PTI instrument and analyzed using FeliX32 software. The solid state films of BODIPY polymeric and copolymeric dyes were prepared by spin-casting methylene chloride solutions of the polymers onto quartz discs [12]. Molecular weights of the polymers were determined by size exclusion chromatography (SEC) 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, HPLC grade THF 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.

2.2. 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. 4,4-Difluoro-8-(4-methoxyphenyl)-1,3,5,7-tetramethyl-4-bora-3a, 4a-diaza-s-indacene (**2**), aldehyde derivative (**4**), 2,6-diethynyl BODIPY derivative (**7**) and 2,5-diiodo-3-decylthiophene (**8**) were prepared according to the reported procedure [10–12].

2.3. 4,4-Difluoro-8-(4-methoxyphenyl)-2,6-diiodo-1,3,5,7tetramethyl-4-bora-3a,4a-diaza-s-indacene (**3**)

lodic acid (11.26 mmol, 1.98 g) in 4 mL of water was added dropwise to the ethanol solution (50 mL) containing BODIPY dye (2) (5.63 mmol 2.0 g) and iodine (6.19 mmol 1.57 g) over 30 min, and stirred for 3 h. The mixture was concentrated under reduced pressure, dissolved in CH₂Cl₂, and washed twice with water and saturated sodium chloride solution. The organic layer was collected, dried over anhydrous Na₂SO₄, and concentrated under reduced



Scheme 2. Synthetic route to BODIPY dyes bearing monostyryl and distyryl groups.

pressure. The crude product was purified according to a reported procedure to yield compound **3** as red crystals (3.2 g, 94%).

2.4. 2,6-Diiodo BODIPY dye bearing monostyryl and distyryl groups (**5**, **6**)

Piperidine (2.88 mL) and acetic acid (2.44 mL) were added to a solution of benzene (120 mL) containing 2,6-diiodo BODIPY dye (3) (1.32 mmol, 800 mg) and aldehyde derivative (4) (5.28 mmol, 1.93 g) in a 250-mL flask. After the mixture was stirred and refluxed by using a Dean Stark trap for 4 h, it was cooled to room temperature and concentrated under reduced pressure. The crude product was dissolved in ethyl acetate and washed twice with water. The organic phase was collected, dried over Na₂SO₄, and filtered. After the filtrate was concentrated, the residue was purified by silica gel column chromatography using hexane/EtOAc (5/1 to 3/1, v/v) to afford dark blue solid compound 5 (540 mg, 43%), dark green solid compound 6 (410 mg, 24%). BODIPY dye bearing monostyryl group (5): ¹H NMR (400 MHz, CDCl₃): δ 8.05 (d, I = 16.8 Hz, 1H), 7.49 (d, I = 16.8 Hz, 1H), 7.26 (d, I = 8.4 Hz, 1H), 7.14 (m, 2H), 7.02 (d, J = 8.0 Hz, 2H), 6.88 (d, J = 8.0 Hz, 1H), 4.18–4.06 (m, 8H), 3.87 (s, 3H), 2.68 (s, 3H), 2.59–2.53 (m, 4H), 2.18–2.13 (m, 4H), 1.48 (s, 3H), 1.44 (s, 3H), 1.26 (t, J = 7.0 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 173.4, 173.3, 160.7, 156.8, 150.5, 149.2, 146.3, 145.2, 140.5, 139.2, 132.8,132.5, 130.4, 129.9, 129.5, 127.1, 121.9, 117.2, 115.1, 113.9, 113.2, 86.3, 82.6, 68.5, 68.2, 60.6, 55.6, 30.9, 24.9, 24.8, 17.9, 17.4, 16.4, 14.5. IR (cm⁻¹): 2924, 1728, 1511, 1468, 1346, 1246, 1164, 1109, 995, 706. ESI-MS: M⁺ (C₄₁H₄₈BF₂I₂N₂O₇) Calcd: m/z = 983.0, Found: m/zz = 980.3. The compound shows absorption maximum at 597 nm and emission maximum at 631 nm in CH₂Cl₂ solution; BODIPY dye bearing distyryl group (**6**): ¹H NMR (400 MHz, CDCl₃): δ 8.04 (d, J = 16.8 Hz, 2H), 7.51 (d, J = 16.4 Hz, 2H), 7.23 (d, J = 9.2 Hz, 2H), 7.17 (d, J = 8.4 Hz, 2H), 7.10 (s, 2H), 7.01 (d, J = 8.4 Hz, 2H), 6.89 (d, J = 8.4 Hz, 2H), 4.15–4.05 (m, 16H), 3.85 (s, 3H), 2.55–2.51 (m, 8H), 2.16–2.09 (m, 8H), 1.46 (s, 6H), 1.27–1.20 (m, 12H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 173.4, 173.3, 160.7, 150.5, 149.1, 145.9, 139.4, 138.9, 133.6, 130.5, 129.8, 127.4, 121.7, 117.3, 115.0, 114.0, 113.7, 83.3, 68.5, 68.2, 60.6, 60.5, 55.6, 30.9, 24.9, 24.8, 17.9, 14.4 ppm. IR (cm⁻¹): 2978, 2933, 1726, 1595, 1509, 1431, 1354, 1244, 1170, 1094, 1010, 770, 708. ESI-MS: M⁺ (C₆₂H₇₆BF₂I₂N₂O₁₃ + Na) Calcd: *m*/*z* = 1381.8. The compound displays absorption maximum at 665 nm and emission maximum at 701 nm in CH₂Cl₂ solution.

2.5. Polymer A

BODIPY dye bearing monostyryl groups (**5**) (0.15 mmol, 150 mg), 2,6-diethynyl BODIPY dye (**7**) (0.18 mmol, 169 mg), and Cul (3 mg) were added to a 100-mL three-neck flask under a nitrogen atmosphere. Pd(PPh₃)₄ (6 mg) was added to the flask in a glove box under a nitrogen atmosphere. When degassed anhydrous THF (40 mL) and diisopropylamine (40 mL) were added to the flask under a nitrogen atmosphere, the resulting mixture was stirred under reflux for 24 h. After removal of the solvent, the residue was dissolved in 250 mL of methylene chloride and washed with water three times. After the organic layer was collected, dried over anhydrous MgSO₄, and filtered, the filtrate was concentrated under reduced pressure and added to 250 mL of ethanol to precipitate the polymer. The precipitated solid was collected, washed with ethanol



Scheme 3. Synthetic route to near-infrared emissive BODIPY polymeric dyes.



Scheme 4. Synthetic rout to near-infrared and deep-red emissive BODIPY copolymeric dyes (polymers C and D).

and hexane, and dried under vacuum for 24 h at room temperature to obtain dark-violet solid (0.202 g). ¹H NMR (400 MHz, CDCl₃): δ 8.19 (br. d, 1H), 7.56 (br. d, 1H), 7.16–7.10 (br. m, 4H), 7.02–7.00 (br. m, 2H), 6.84 (br. d, 1H), 6.42 (br. s, 2H), 4.14–4.06 (br. m, 8H), 3.98 (br. m, 2H), 3.86 (br. m, 7H), 2.68–2.64 (br. m, 9H), 2.57–2.52 (br. m, 4H), 2.18–2.13 (br. m, 4H), 1.76 (br. m, 6H), 1.66 (br. s, 6H), 1.54–1.23 (br. m, 66H), 0.86–0.85 (br. m, 9H). IR (cm⁻¹): 2922, 2852, 1734, 1509, 1313, 1228, 1164, 1086, 1000, 759. SEC (THF, polystyrene standard), *M*_n: 35.5 × 10³ g/mol; polydispersity: 2.3. The polymer shows absorption maximum at 697 nm and emission maximum at 715 nm in CH₂Cl₂ solution.

2.6. Polymer B

2,6-Diiodo BODIPY dye bearing distyryl groups (**6**) (0.11 mmol, 150 mg), 2,6-diethynyl BODIPY dye (**7**) (0.13 mmol, 122 mg), and CuI (3 mg) were added to a 100-mL three-neck flask under a nitrogen atmosphere. Pd(PPh₃)₄ (6 mg) was added to the flask in the glove box under a nitrogen atmosphere. After degassed anhydrous THF (40 mL) and diisopropylamine (40 mL) were added to the flask under a nitrogen atmosphere, the mixture was stirred under reflux for 24 h. Polymer **B** was purified by using the procedure for polymer **A** to obtain dark-violet solid (0.182 g). ¹H NMR (400 MHz, CDCl₃): δ 8.20 (br. d, 2H), 7.63 (br. d, 2H), 7.16–7.10 (br. m, 4H), 7.03 (br. s, 2H), 7.02 (br. d, 2H), 6.88 (br. d, 2H), 6.43 (br. s, 2H), 4.15–4.08 (br. m, 16H),

3.99 (br. m, 2H), 3.87 (br. m, 7H), 2.66 (br. s, 6H), 2.57–2.52 (br. m, 8H), 2.18–2.14 (m, 8H), 1.76 (br. m, 6H), 1.66 (br. s, 12H), 1.56–1.23 (br. m, 66H), 0.86–0.85 (br. m, 9H) ppm. 13 C NMR (100 MHz, CDCl₃): δ 173.4, 173.3, 160.7, 154.5, 152.3, 150.7, 149.2, 144.6, 143.4, 139.1, 133.5, 131.5, 130.4, 125.2, 122.1, 117.4, 114.9, 113.9, 113.2, 106.3, 94.6, 91.5, 74.0, 69.8, 68.6, 68.2, 60.6, 60.5, 55.5, 32.1, 31.8, 30.9, 30.5, 29.9, 29.8, 29.5, 26.4, 26.2, 24.9, 24.8, 23.6, 22.9, 14.4, 14.3 ppm. IR (cm⁻¹): 2921, 2852, 1733, 1506, 1313, 1238, 1179, 1082, 1004, 758, 709. SEC (THF, polystyrene standard), M_n : 45.1 × 10³ g/mol; polydispersity: 2.4. The polymer shows absorption maximum at 738 nm and emission maximum at 760 nm in CH₂Cl₂ solution.

2.7. Compound 9

2,5-Diiodo-3-decylthiophene (**8**) (4.20 mmol, 2 g), Cul (4 mg), and $Pd(PPh_3)_2Cl_2$ (10 mg) were added to a 100-mL three-neck flask under a nitrogen atmosphere. After degassing anhydrous THF (20 mL), diisopropylamine (20 mL), and trimethylsilylacetylene (12.6 mmol, 1.2 g) were added to the flask under a nitrogen atmosphere, the mixture was stirred at room temperature for 12 h. The mixture was concentrated, dissolved in 50 mL of CH₂Cl₂ and washed twice with water and saturated saline solution. When the organic layer was collected, dried over anhydrous MgSO₄, and filtered, the filtrate was purified by silica gel column chromatography using hexane/EtOAc



Scheme 5. Synthetic route to red emissive BODIPY copolymeric dye.



Fig. 1. ¹H NMR spectra of BODIPY monomeric dyes (5, 7) and polymeric dye (polymer A) in CDCl₃ solution.



Fig. 2. ¹H NMR spectra of BODIPY monomeric dyes (6, 7) and polymeric dye (polymer B) in CDCl₃ solution.



Fig. 3. Absorption spectra of BODIPY dyes (2, 3, 5, 6 and 7) and polymeric dyes (polymers A and B), their thin films.

(98/2 v/v) to yield viscous liquid (1.46 g, 84%). ¹H NMR (400 MHz, CDCl₃): δ 6.94 (s, 1H), 2.59 (t, *J* = 7.6 Hz, 2H), 1.56 (t, *J* = 6.8 Hz, 2H), 1.31–1.26 (m, 14H), 0.87 (t, *J* = 6.8 Hz, 3H), 0.19 (s, 18H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 148.6, 133.6, 122.9, 120.1, 101.9, 99.6, 97.6, 97.1, 32.1, 30.1, 29.8, 29.7, 29.5, 29.3, 22.9, 14.3, 0.09 ppm.

2.8. 2,5-Diethynyl-3-decylthiophene (10)

Tetrabutylammonium fluoride (5.63 mmol 2.0 g) was added to the degassed solution of compound **9** (12.1 mmol, 0.50 g) in dry THF (50 mL) at -70 °C through syringe and the resulting mixture was stirred at room temperature for 2 h. After the reaction was quenched with dilute acetic acid and 50 mL of dichloromethane was added to the flask, the mixture was washed twice with water and saturated saline solution. When the organic layer was collected, dried over anhydrous MgSO₄, and filtered, the filtrate was concentrated. The residue was purified by column chromatography using hexane/EtOAc (95/5 v/v) to yield yellow liquid (0.28 g, 87%). The compound was immediately stored at 4 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.00 (s, 1H), 3.42 (d, *J* = 1.2 Hz, 1H), 3.30 (d, *J* = 0.8 Hz, 1H), 2.63 (t, *J* = 7.0 Hz, 2H), 1.58(t, *J* = 7.0 Hz, 2H), 1.31–1.27 (m, 14H), 0.89 (t, *J* = 6.4 Hz, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 148.8, 133.9, 122.3, 119.1, 84.2, 81.9, 76.9, 76.2, 32.2, 30.2, 29.9, 29.8, 29.6, 29.5, 29.4, 22.9, 14.4 ppm.

2.9. Polymer C

2,5-Diiodo BODIPY dye bearing distyryl groups (**6**) (0.11 mmol, 150 mg), 2,5-diethynyl-3-decylthiophene (**10**) (0.14 mmol, 36 mg), and CuI (3 mg) were added to a 100-mL three-neck flask under a nitrogen atmosphere. Pd(PPh₃)₄ (6 mg) was added to the flask in the glove box under a nitrogen atmosphere. When degassed anhydrous THF (40 mL) and diisopropylamine (40 mL) were added to the flask under reflux for 24 h, concentrated and added dropwise to 250 mL of ethanol under stirring to precipitate the polymer. The precipitated polymer was collected, washed with water, ethanol, acetone and hexane and dried under vacuum for 24 h at room temperature to afford dark-violet solid (0.113 g). ¹H NMR (400 MHz, CDCl₃): δ 8.22 (br. d, 2H), 7.65 (br. d, 2H), 7.16–7.10 (br. m, 4H), 7.05 (br. s, 2H), 7.02 (br. m, 3H), 6.89 (br. d, 2H), 4.15–4.08 (br. m, 16H), 3.87 (br. s, 3H),

2.67–2.63 (br. m, 10H), 2.16–2.09 (br. m, 8H), 1.58 (br. t, 2H), 1.46 (br. s, 6H), 1.30–1.20 (br. m, 26H), 0.87 (br. t, 3H) ppm. IR (cm⁻¹): 2921, 2852, 1732, 1509, 1457, 1262, 1249, 1175, 1135, 1044, 958, 750, 723. SEC (THF, polystyrene standard), $M_{\rm n}$: 32.1 × 10³ g/mol; polydispersity: 2.2. The polymer **C** shows absorption maximum at 713 nm and emission maximum at 758 nm in CH₂Cl₂ solution.

2.10. Polymer **D**

2,5-Diiodo BODIPY dye bearing monostyryl group (5) (0.10 mmol, 100 mg), diethynyl-3-decylthiophene (10) (0.12 mmol, 34 mg), and CuI (3 mg) were added to a 100-mL three-neck flask under a nitrogen atmosphere. Pd(PPh₃)₄ (6 mg) was added to the flask in the glove box under a nitrogen atmosphere. Degassed anhydrous THF (40 mL) and anhydrous diisopropylamine (40 mL) were added to the flask under a nitrogen atmosphere, and the mixture was stirred under reflux for 24 h. The polymer **D** was purified by using the same procedure for polymer **C** to afford darkviolet solid (0.082 g). ¹H NMR (400 MHz, CDCl₃): δ 8.17 (br. d. 1H). 7.54 (br. d. 1H), 7.15–7.08 (br. m. 4H), 7.02–6.98 (br.m. 3H), 6.82 (br. d, 1H), 4.12-4.03 (br. m, 8H), 3.87 (br.s, 3H), 2.67-2.63 (br. m, 5H), 2.58-2.51 (br. m, 4H), 2.16-2.13 (br. m, 4H), 1.58 (br. t, 2H), 1.48–1.24 (br. m, 26H), 0.88 (br. t, 3H) ppm. IR (cm⁻¹): 2921, 2851, 1732, 1509, 1403, 1247, 1178, 1022, 1007, 835. SEC (THF, polystyrene standard), $M_{\rm n}$: 22.4 × 10³ g/mol; polydispersity: 2.1. The polymer **D** shows absorption maximum at 649 nm and emission maximum at 694 nm in CH₂Cl₂ solution (Scheme 5).

2.11. Polymer E

2,6-Diethynyl BODIPY dye (**7**) (0.14 mmol, 150 mg), 2,5-diiodo-3-decylthiophene (**8**) (0.12 mmol, 60 mg), and CuI (3 mg) were added to a 100-mL three-neck flask under a nitrogen atmosphere. Pd(PPh₃)₄ (6 mg) was added to the flask in the glove box under a nitrogen atmosphere. Anhydrous THF (40 mL) and diisopropylamine (40 mL) were added to the flask in a nitrogen atmosphere. After stirring under reflux for 24 h, the reaction mixture was added dropwise to 500 mL of ethanol to precipitate the polymer. The precipitated polymer was collected, washed with water, ethanol, acetone and hexane and dried under vacuum for 24 h at room temperature to obtain dark-violet solid (0.132 g). ¹H NMR



Fig. 4. Fluorescence spectra of BODIPY dyes (2, 3, 5, 6 and 7) and polymeric dyes (polymers A and B).

Table 1

Absorption and emission maxima, fluorescence quantum yields and lifetimes of BODIPY monomeric and polymeric dyes in methylene chloride solution.

BODIPY dyes or polymers	2	3	5	6	7	Α	В	С	D	Е
Absorption maxima (nm)	500	533	597	665	539	697	738	713	649	634
Emission maxima (nm)	510	548	631	701	554	715	760	758	694	669
Quantum yield (%)	80	5.7	2.6	4	52	11	13	1.3	1.1	1.2
Fluorescence lifetime (ns)	3.8	1.7	1.7	2.3	3.0	0.86	0.71	0.52	0.69	0.41

(400 MHz, CDCl₃): δ 6.95 (br.s, 1H), 6.45 (br. s, 2H), 4.02 (br. s, 2H), 3.91 (br. s, 4H), 2.67 (br. s, 6H), 1.77(br. t, 4H), 1.64 (br.s, 6H), 1.49–1.44 (br. m, 6H), 1.24 (br. m, 72H), 0.85 (br. t, 12H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 158.7, 154.6, 147.5, 143.2, 142.5, 139.2, 132.4, 131.5, 115.8, 106.3, 90.2, 88.8, 73.9, 69.7, 32.2, 32.1, 30.5, 30.3, 29.9, 29.8, 29.6, 29.5, 26.3, 26.2, 22.9, 14.3, 13.9, 13.5 ppm. IR (cm⁻¹): 2921, 2852, 1525, 1315, 1229, 1111, 1004, 759, 720. SEC (THF, polystyrene standard), *M*_n: 20.8 × 10³ g/mol; polydispersity: 2.2. The polymer **E** shows absorption maximum at 634 nm and emission maximum at 669 nm in CH₂Cl₂ solution.

3. Results and discussion

3.1. Synthesis of BODIPY monomeric, polymeric and copolymeric dyes

We have prepared deep-red emissive BODIPY polymeric dyes with emission maxima of up to 698 nm by palladium-catalyzed Sonogashira coupling of 2,6-diiodo BODIPY dyes with 2,6-ethynyl BODIPY dyes [10,12]. In order to tune fluorescence of BOIDPY polymeric dyes into the near-infrared region, we extended the π conjugation of BODIPY monomeric dyes by introducing styryl groups at the 3,5 positions of BODIPY dyes (Scheme 2). Meso-arylsubstituted BODIPY dye (2) was prepared through the condensation of 4-methoxybenzaldehyde (1) with 2,4-dimethylpyrrole in the presence of a catalytic amount of trifluoroacetic acid (TFA), and followed by oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and chelation with BF3-etherate in the presence of N,N-diisopropylethylamine (DIEA). Further iodinization of BODIPY dye 2 at its 2,6 positions afforded 4,4-difluoro-8-(4-methoxyphenyl)-2,6-diiodo-1,3,5,7-tetramethyl-4-bora-3a, 4a-diaza-sindacene (3). Condensation of BODIPY dye 3 bearing methyl substituents on 3 and 5 positions with aldehyde derivative (4) afforded BODIPY dyes bearing one, two styryl groups (5, 6) (Scheme 2). Ethyl esters were introduced to BODIPY monomers at 3.5 positions to facilitate easy separation of BODIPY monomers bearing one or two styryl groups (5, 6) and provide a future potential use of the ester-functionalized side chains as cell-trappable biosensors [12]. Yields of BODIPY monomers bearing one or two styryl groups (5, 6) can be manipulated by controlling reaction time and ratio of BODIPY dye 3 to aldehyde derivative (4). Increase of reaction time (to 5 h) and ratio (1:7) of BODIPY dye **3** to aldehyde deriviative (4) increases yield (up to 33%) of BODIPY monomer bearing two styryl groups (6). Tridodecyloxy groups were introduced to BODIPY monomer (7) at the meso-position to enhance solubility of BODIPY polymers in organic solvents. Near-infrared

Table 2

Absorption and emission maxima of thin films on quartz surface.

BODIPY polymers	Thin film polymer A	Thin film polymer B	Thin film polymer E
Absorption maxima (nm)	759	784	706
Emission maxima (nm)	769	810	727

emissive BODIPY polymeric dyes (polymers A and B) were prepared by palladium-catalyzed Sonogashira polymerization of monostyryland distyryl-substituted BODIPY dyes (5, 6) with 2,6-diethynyl BODIPY dye (7), respectively (Scheme 3). Both polymers A and B are readily soluble in common organic solvents such as dichloromethane, chloroform, and THF. However, polymer **B** has higher solubility than polymer A because of its distyryl groups. To further demonstrate the potential tuning of the polymer fluorescence and synthetic diversity, we incorporated a thiophene unit into the BODIPY-based polymer backbone and prepared near-infrared and deep-red emissive BODIPY copolymeric dyes (polymers **C** and **D**) (Scheme 4). 2,5-Diethynyl-3-decylthiophene (10) was prepared by Sonogashira coupling reaction of 2,5-diiodo-3-decylthiophene (8) with ethynyltrimethylsilane to give compound 9, and followed by hydrolysis of compound **9** in the presence of tetrabutylammonium fluoride in THF (Scheme 4). The BODIPY copolymeric dyes (polymers **C** and **D**) were prepared by palladium-catalyzed Sonogashira polymerization of distyryl- and monostyrul-substituted BODIPY dyes (6, 5) with 2,5-diethynyl-3-decylthiophene (10), respectively. These BODIPY copolymeric dyes (polymers **C** and **D**) have lower solubility in common organic solvents such as methylene chloride, chloroform, and THF than polymers A and B. For comparison in optical properties, we prepared red emissive BODIPY copolymeric dye (polymer E) by palladium-catalyzed Sonogashira polymerization of 2,6-diethynyl BODIPY dyes (7) with 2,5-diiodo-3-decylthiophene (8). Polymer E is highly soluble in solvents such as methylene chloride, chloroform and THF.

¹H and ¹³C NMR spectroscopy studies confirm the molecular structures of polymers **A** and **B** (Scheme 1). ¹H NMR spectral peaks of polymers **A** and **B** are slightly broader than those of its BODIPY monomers (**5**, **6** and **7**) (Figs. 1 and 2). All peaks corresponding to BODIPY monomers are readily observed in the ¹H NMR spectra of the polymers except for the singlet proton at 3.30 ppm



Fig. 5. Absorption and fluorescence spectra of BODIPY copolymeric dyes.



Fig. 6. TGA curves for the BODIPY-based polymers (A, B, C, D).

corresponding to the ethynyl protons in 2,6-diethynyl BODIPY dye (**7**) (Fig. 1), which further confirms Sonogashira polymerization via the C–C triple bond. A similar result was also observed in ¹H NMR spectrum of polymer **B** (Fig. 2).

3.2. Optical properties of BODIPY polymeric and copolymeric dyes

The photophysical characteristics of BODIPY intermediate, monomeric, and polymeric dyes were investigated in methylene chloride. The absorption properties of the BODIPY dye 2 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 due to the $S_0 \rightarrow S_2 (\pi - \pi^*)$ transition [20] (Fig. 4). The introduction of diiodo substituent to the dipyrromethene core (2) results in a significant red shift (up to 33 nm and 38 nm) of both the absorption and emission maxima of BODIPY dye **3** corresponding to $S_0 \rightarrow S_1 (\pi - \pi^*)$ transition (Figs. 3 and 4), and significantly quenches the fluorescence because of the heavy atom effect (Table 1). Absorption and fluorescence spectra of 2,6diiodo-substituted BODIPY dye 3 exhibit good mirror symmetry with similar band shapes for the absorption and emission spectra which was also verified by measuring their full width at halfmaximum (Figs. 3 and 4). Further condensation of 2,6-diiodo BODIPY dye bearing methyl substituents at 3 and 5 positions (3) with aldehyde derivative (4) gave longer wavelength absorbing BODIPY dyes bearing alkoxymonostyryl and alkoxydistyryl groups (5, 6). The extended π -conjugation in these dyes results in significant red shifts in both absorption and emission spectra compared with their precursor BODIPY dye (3). Monostyryl-substituted BODIPY dye (5) shows absorption and emission maxima at 579 nm and 631 nm with red shifts of 79 nm and 121 nm in absorption and emission spectra, respectively, compared with its starting BODIPY dye (2). Distyryl-substituted BODIPY dye (6) displays further red shifts of 165 nm and 170 nm in absorption and emission spectra with absorption and emission maxima of 665 nm and 701 nm, respectively, compared with its starting BODIPY dye (2) (Table 1). Both monostyryl and distyryl-substituted BODIPY dyes (5, 6) exhibit low fluorescence quantum yields because of the heavy atom effect. Palladium-catalyzed Sonogashira polymerization of BODIPY dyes (5, 6) with 2,6-diethynyl-substituted BODIPY (7) resulted in near-infrared emissive BODIPY polymeric dyes (polymers A and B) with significant extension of π -conjugation, relative to their monomeric dye (5). Polymer A shows dramatic red shifts of 100 nm and 84 nm in absorption and emission with maxima of 679 nm and 715 nm respectively. Polymer **B** displays absorption and emission maxima at 738 nm and 760 nm with significant red shifts of 73 nm and 59 nm respectively, compared with its distyryl-substituted BODIPY monomeric dye (**6**) (Figs. 3 and 4).

Palladium-catalyzed Sonogashira polymerization of distyryland monostyryl-substituted BODIPY dyes (**6**, **5**) with 2,5-diethynyl-3-decylthiophene (**10**) resulted in near-infrared and deep-red emissive BODIPY copolymeric dyes with emission maxima of 758 nm and 694 nm (polymers **C** and **D**), respectively (Fig. 5). Palladium-catalyzed Sonogashira polymerization of 2,6diethynyl-substituted BODIPY dyes (**7**) with 2,5-diiodo-3decylthiophene (**8**) resulted in red emissive BODIPY copolymeric dye with emission maxima of 634 nm and 669 nm (polymer **E**). All BODIPY copolymeric dyes display low fluorescence quantum yields because of heavy sulfur atom effect (Table 1). Lifetimes of BODIPY polymeric dyes are shorter than their monomeric dyes (Table 1).

Solid state absorption and emission spectra were collected to evaluate the effect of polymer aggregation on the optical properties as the absorption and emission spectra of the film reflect $\pi - \pi$ stacking effects between polymer backbones. The absorption spectra of the polymers in thin films became a little broader, and maximum peaks were obviously red-shifted compared with those in methylene chloride solutions. The fluorescence spectra of the polymers in solid state thin films retain most of the spectra features in solution and exhibit further red shifts of their absorption and emission maxima compared with those in methylene chloride solution, indicating the presence of intermolecular electronic interactions and/or increase in coplanarity of the polymer in the solid state (Table 2).

3.3. Thermal stabilities of the polymers

Thermal stabilities of BODIPY polymeric and copolymeric dyes were evaluated by thermogravimetric analysis (TGA) at the heating rate of 20 °C/min under nitrogen atmosphere. The thermograms show that polymers **A**, **B** and **C** lost 5% of their weight at 250 °C (the decomposition temperature (T_d) that corresponds to weight loss of 5%), which suggests good thermal stability (Fig. 6). Clear phase transition in differential scanning calorimetry (DSC) of polymers was not observed, which may arise because the rigid backbone of the BODIPY causes transition temperatures greater than its decomposition temperatures or because the glass transitions are very broad.

4. Conclusion

We have successfully synthesized new near-infrared emissive BODIPY polymeric and copolymeric dyes (polymer **A**, **B** and **C**) by palladium-catalyzed Sonogashira polymerization of BODIPY dyes substituted with one and two styryl groups (5, 6) with 2,6-diethynyl-substituted BODIPY (7), and BODIPY dye bearing two styryl groups (6) with 2,5-diethynyl-3-decylthiophene (9), respectively. 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. By analogous synthetic approaches a variety of functional groups such as cancer-homing peptides and carbohydrates could be introduced through long flexible oligo(ethylene glycol) tethered spacers to near-infrared emissive BODIPY polymeric and copolymeric dyes at the meso-position of BODIPY cores for near-infrared imaging biomedical applications. We will report these results in due course.

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References

- [1] Ulrich G, Ziessel R, Harriman A. Angew Chem Int Ed 2008;47:1184-201.
- [2] Loudet A, Burgess K. Chem Rev 2007;107:4891–932.
- [3] Ziessel R, Ulrich G, Harriman A. New J Chem 2007;31(4):496-501.
- [4] Martin K, Hart C, Schulenberg B, Jones L, Patton WF. Proteomics 2002; 2(5):499-512.
- [5] Erten-Ela S, Yilmaz MD, Icli B, Dede Y, Icli S, Akkaya EU. Org Lett 2008; 10(15):3299–302.

- [6] Huh JO, Do Y, Lee MH. Organometallics 2008;27(6):1022-5.
- [7] Hudnall TW, Gabbai FP. Chem Commun 2008;38:4596-7.
- [8] Atilgan S, Ozdemir T, Akkaya EU. Org Lett 2008;10(18):4065-7.
 [9] Zheng OD, Xu GX, Prasad PN. Chem Eur | 2008;14(19):5812-9.
- [10] Donuru VR, Vegesna GK, Velayudham S, Green S, Liu HY. Chem Mater 2009;
- 21(10):2130–8.
- [11] Meng G, Velayudham S, Smith A, Luck R, Liu HY. Macromolecules 2009; 42(6):1995–2001.
- [12] Donuru VR, Vegesna GK, Velayudham S, Meng G, Liu HY. J Polym Sci Part A Polym Chem 2009;47(20):5354–66.
- [13] Cakmak Y, Akkaya EU. Org Lett 2009;11(1):85–8.
- [14] Kim B, Ma B, Donuru VR, Liu H, Frechet JMJ. Chem Commun (Camb) 2010; 46(23):4148-50.
- [15] Nagai A, Chujo Y. Macromolecules 2010;43(1):193-200.
- [16] Parker CA, Rees WT. Analyst 1960;85:587–600.
- [17] Yogo T, Urano Y, Ishitsuka Y, Maniwa F, Nagano T. J Am Chem Soc 2005; 127(35):12162-3.
- [18] Maruyama S, Kikuchi K, Hirano T, Urano Y, Nagano T. J Am Chem Soc 2002;124(36):10650-1.
- [19] Gabe Y, Urano Y, Kikuchi K, Kojima H, Nagano T. J Am Chem Soc 2004; 126(10):3357–67.
- [20] Goncalves MST. Chem Rev 2009;109(1):190–212.