Post-Polymerization Functionalization Approach for Highly Water-Soluble Well-Defined Regioregular Head-to-Tail Glycopolythiophenes

Cuihua Xue,[†] Fen-Tair Luo,[‡] and Haiying Liu*,[†]

Department of Chemistry, Michigan Technological University, 1400 Townsend Drive, Houghton, Michigan 49931, and Institute of Chemistry, Academia Sinica, Taipei, Taiwan 115, Republic of China

Received April 20, 2007; Revised Manuscript Received July 6, 2007

ABSTRACT: Two bromide-bearing regioregular head-to-tail polythiophenes (polymers **1** and **3**) were prepared by using Grignard metathesis method to polymerize 2,5-dibromo-3-bromohexylthiophene (**2**) and 2,5-dibromo-3-(11-bromo-3,6,9-trioxa-1-undecoxy)thiophene (**7**), respectively. Well-defined regioregular head-to-tail glycopolythiophenes were prepared through post-polymerization functionalization approach by treating the bromide-bearing polythiophenes with 1-thiolethyl-α-D-mannose tetraacetate (**3a**) or 1-thiol-β-D-glucose tetraacetrate (**3b**) in THF solution with a basic condition, respectively, and followed by sequential deacetylation under Zemplén conditions in methanol and methylene chloride containing sodium methoxide at room temperature. Glycopolythiophenes (polymers **C** and **D**) with hydrophilic tetra(ethylene glycol) as tethered spacers between the polymer backbone and carbohydrate residues are highly water-soluble while glycopolythiophenes (polymers **A** and **B**) with hydrophobic hexyl tethered spacers are completely insoluble in water. All polythiophenes display low fluorescence with fluorescent quantum yield ranging from 0.4% to 3%. However, water-soluble polymers **C** and **D** in 0.1 M phosphate buffer (pH 7.2) show a little higher fluorescent intensity than their precursor polymer **3** in chloroform solution. α-Mannose-bearing glycopolythiophene (polymer **C**) exhibits specific binding to Concanavalin A through multivalent interactions with a binding constant of 2.15×10^5.

Introduction

Carbohydrates play important roles in key recognition events with a variety of receptor proteins such as hormones, enzymes, toxins, lectins, antibodies, viruses, and bacteria. They are also involved in numerous biological processes such as cell growth, recognition and differentiation, cancer metastasis, inflammation, and bacterial and viral infection.[1−3] These specific interactions occur through glycoproteins, glycolipids, and polysaccharide displays found on cell surfaces and proteins with carbohydrate-binding domains called lectins through cooperative multiple interactions since it is known that individual carbohydrate-protein interactions are generally weak.[3,4] Fluorescent conjugated glycopolymers, which combine fluorescent scaffolding and carbohydrate reporting functions into one package, provide very useful means to study carbohydrate−protein interaction for biosensing applications because of their intrinsic fluorescence and high sensitivity to minor external stimuli due to amplification by a cooperative system response.[5−10] A few fluorescent conjugated glycopolymers such as poly(*p*-phenylene−ethynylene) (PPE) and polythiophene derivatives have been prepared through prepolymerization and post-polymerization functionalization approaches.[11−13] PPEs bearing α-mannose or β-glucose residues have been prepared through prepolymerization functionalization approach by polymerizing well-defined carbohydrate-carrying monomers.[11,14] An alternative synthetic method has been used to prepare PPEs bearing α-D-mannose or α-D-galactose residues by post-polymerization functionalization of carboxylic acid-bearing PPE with amine-bearing carbohydrates via an amidation reaction.[12,13] The post-polymerization functionalization is generally advantageous because it provides a versatile approach to rapidly attach a variety of carbohydrates to conjugated polymers and to easily control a functionalization degree of carbohydrates along the polymer chain.[13] However, incomplete reactions with the functional groups along the polymer chain may result in polymers with not well-defined structures. Neutral PPEs bearing carbohydrate pendants display low water solubility,[14] probably due to strong $\pi-\pi$ stacking interactions among hydrophobic PPE backbones. Introduction of anionic groups such as carboxylic acid to PPE significantly enhances water solubility of carbohydrate-bearing PPEs and prevent the $\pi-\pi$ stacking interactions of PPE backbones via charge repulsion.[15] However, the presence of ionic groups in conjugated polymers might cause interfering responses due to nonspecific electrostatic interactions in complicated biological samples.[15] Therefore, it is important to explore general and simple approaches to prepare a variety of highly water-soluble neutral fluorescent conjugated glycopolymers with well-defined structures to study protein-carbohydrate interactions.

We have successfully employed prepolymerization and post-polymerization functionalization approaches to synthesize water-soluble well-defined fluorescent conjugated glycopoly-(p-phenylene)s and fluorene-based conjugated glycopolymers through thioether bridges.[16,17] In this article, we extend the post-polymerization functionalization approach to prepare four well-defined regioregular head-to-tail glycopolythiophenes bearing β-D-glucose or α-D-mannose residues by further functionalizing bromide-bearing polythiophenes (polymers **1** and **3**) with thiol-functionalized carbohydrate derivatives as polythiophenes represent an important class of conjugated polymers which have been found in variety of sensing applications for metal ions, proteins, virus, and DNAs.[8,18−21] Glycopolythiophenes bearing β-D-glucose or α-D-mannose residues through hexyl tethers (polymers **A** and **B**) are insoluble in water due to hydrophobic feature of the tethered groups. However, the water solubility of

* Corresponding author. E-mail: hyliu@mtu.edu.
[†] Department of Chemistry, Michigan Technological University.
[‡] Institute of Chemistry, Academia Sinica.

10.1021/ma070927k CCC: $37.00
Published on Web 08/28/2007

the glycopolythiophenes (polymers **C** and **D**) have been easily achieved by using oligo(ethylene glycol) tethered spacers between carbohydrates and the polymer backbone. Titration of concanavalin A (Con A) to α-mannose-bearing polymer **C** resulted in significant fluorescent quenching of the polymer with Stern−Volmer quenching constant of 2.15×10^5 while titration of Con A to a phosphate buffer solution containing β-glucose-bearing polymer **D** shows no significant change in the polymer fluorescence. The post-polymerization functionalization approach will provide a facile and versatile way to rapidly attach a variety of carbohydrates to conjugated polymers for well-defined conjugated glycopolymers for potential biosensing applications for cells and viruses.

Experimental Section

Instrumentation. ^{1}H NMR and ^{13}C NMR spectra were taken on 400 MHz Varian Unity Inova spectrophotometer. ^{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−visible spectrophotometer. Fluorescence spectra were obtained on a Spex Fluorolog 1681 0.22 m steady-state fluorometer. Fluorescent quantum yield of the polymers was determined by using quinine sulfate in 0.1 N sulfuric acid as the reference absolute quantum efficiency (ϕ_n = 55%).[22] 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. Polymer solutions were prepared in THF and filtered through a 50 μM filter before injection. Molecular weight was measured relative to polystyrene standards.

Materials. Unless otherwise indicated, all reagents and solvents were obtained from commercial suppliers (Aldrich, Fluka, Acros, 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 argon. 3-Bromohexylthiophene,[23] and 1-thiol-ethyl-α-D-mannose tetraacetate (**3a**)[24] were prepared and characterized according to literature.

Preparation of 2,5-Dibromo-3-bromohexylthiophene (2). 2,5-Dibromo-3-bromohexylthiophene was prepared according to a modified procedure of the literature.[23] Freshly recrystallized *N*-bromosuccinimide (NBS) (3.75 g, 21.06 mmol) was added to a mixture consisting of THF (15 mL), acetic acid (15 mL) and 3-bromohexylthiophene (**1**) (2.60 g, 10.53 mmol). After the resulting solution was stirred for 1.5 h at room temperature, it was added to 100 mL of water and extracted with EtOAc (3 × 20 mL). The combined organic layer was washed with saturated NaCl solution (3 × 50 mL), dried over anhydrous $MgSO_4$, filtered and concentrated at a reduced pressure. The crude compound was purified by column chromatography on silica gel with hexane as a mobile phase to give the target compound (3.19 g, 74.9% yield) as a colorless oil.[23] ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.76 (s, 1H), 3.40 (t, J = 7.0 Hz, 2H), 2.52 (t, J = 7.0 Hz, 2H), 1.87 (m, 2H), 1.41−1.55 (m, 6H) ppm.

Preparation of Poly(3-bromohexylthiophene) (Polymer 1). Regioregular head-to-tail poly(3-bromohexylthiophene) was prepared according to a reported procedure.[23] 3-Bromohexyl-2,5-dibromothiophene (**2**) (2.02 g, 5.0 mmol) was added to 30 mL of dried THF containing CH_3MgBr (1.7 mL, 5 mmol). Ni(dppp)Cl_2 (14 mg, 0.03 mmol) was added after the mixture was stirred at 75 °C for 2 h. When the mixture was further stirred at 75 °C for 1 h, the resulting solution was cooled to room temperature and poured into 200 mL of methanol to precipitate the polymer. The solid polymer was filtered, further purified by extraction in a Soxhlet extractor with refluxing methanol for 24 h, and dried under vacuum to give 0.9 g of 98% regioregular head-to-tail coupled polymer **1**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.97 (s, 1H), 3.41 (t, J = 6.8 Hz, 2H), 2.81 (m, 2H), 1.87 (m, 2H), 1.71 (m, 2H), 1.48 (m. 4H) ppm. GPC (THF, polystyrene standard), M_n: 25 900 g/mol; polydispersity: 1.75. It displays UV−visible absorption maxima at 400 nm and emission maxima at 558 nm in chloroform solution.

Preparation of Polymer 2a. Poly(3-bromohexylthiophene) (polymer **1**) (0.2 g), 1-thiolethyl-α-D-mannose tetraacetate (**3a**) (0.6 g, 1.47 mmol) and potassium carbonate (0.45 g, 3.27 mmol) were placed in a 50 mL round-bottom flask. THF (40 mL) was added to the flask and the mixture was stirred at room temperature for 48 h. When the solvent was removed, the residue was diluted with methylene chloride (50 mL) and washed with water (3 × 200 mL). The organic layer was collected, dried over anhydrous $MgSO_4$, and filtered. The filtrate was concentrated and added to methanol to precipitate the polymer. The resulting polymer was collected by filtration, further purified by extraction in a Soxhlet extractor with refluxing methanol for 3 h, and dried under a vacuum overnight to afford the product (0.41 g, 88% yield) as a light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.96 (s, 1H), 5.26 (m, 3H), 4.83 (s, 1H), 4.26 (m, 1H), 4.10 (m, 2H), 3.77 (m, 2H), 2.79 (m, 2H), 2.71 (m, 2H), 2.56 (m, 2H), 2.13 (s, 3H), 2.08 (s, 3H), 2.02 (s, 3H), 1.96 (s, 3H), 1.69 (m, 2H), 1.62 (m, 2H), 1.45 (m, 4H) ppm. It displays absorption maxima at 400 nm and emission maxima at 556 nm in chloroform solution.

Preparation of Polymer A. Solution of 0.5 M CH_3ONa (1 mL) was added to a mixture consisting of dry CH_2Cl_2 (5 mL), CH_3OH (10 mL), and polymer **2a** (0.2 g). After the resulting mixture was stirred at room temperature for 24 h, the solution was concentrated at a reduced pressure and added to methanol to precipitate the polymer. The resulting polymer was separated by filtration, washed with water and methanol 3 times, respectively, and dried under vacuum to give the product (0.11 g) as a dark red solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.13 (s, 1H), 5.03 (m, 3H), 4.82 (s, 1H), 4.58−4.41 (m, 2H), 4.28 (m, 1H), 3.73 (m, 2H), 3.40−3.47 (m, 4H), 2.79 (m, 2H), 2.72 (m, 2H), 2.57 (m, 2H), 1.62 (m, 2H), 1.53 (m, 2H), 1.38 (m, 4H) ppm. It displays absorption maxima at 400 nm and emission maxima at 556 nm in DMSO solution.

Preparation of Polymer 2b. Polymer **1** (0.2 g, 0.82 mmol), 1-thiol-β-D-glucose tetraacetrate (**3b**) (0.40 g, 1.09 mmol), and potassium carbonate (0.45 g, 3.27 mmol) were placed in a 50 mL round-bottom flask. THF (40 mL) was added to the flask and the mixture was stirred at room temperature for 48 h. After removal of the solvent, the residue was diluted with methylene chloride (50 mL), washed with water (3 × 200 mL), dried over anhydrous $MgSO_4$, and filtered. The filtrate was concentrated at a reduced pressure and poured into methanol to give the precipitated polymer. The crude product was isolated by filtration, further purified by extraction in a Soxhlet extractor with refluxing methanol for 3 h, and dried under a vacuum overnight to give the product (0.39 g, 91% yield) as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.95 (s, 1H), 5.19 (m, 1H), 5.03 (m, 2H), 4.47 (m, 1H), 4.21 (m, 1H), 4.11 (m, 1H), 3.69 (m, 1H), 2.78 (m, 2H), 2.66 (m, 2H), 2.03 (m, 6H), 1.99 (m, 6H), 1.68 (m, 2H), 1.61 (m, 2H), 1.43 (m, 4H) ppm. It exhibits absorption maxima at 400 nm and emission maxima at 556 nm in chloroform solution.

Preparation of Polymer B. Solution of 0.5 M CH_3ONa (1 mL) was added to a mixture consisting of dry CH_2Cl_2 (5 mL), CH_3OH (10 mL) and polymer **2b** (0.2 g). The resulting mixture was stirred at room temperature for 24 h. The solution was concentrated by rotary evaporation and added to methanol to precipitate the polymer. The resulting polymer was isolated by filtration, washed with water and methanol three times, respectively, and dried under vacuum to give the product (0.12 g, 88%) as a dark red solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.13 (s, 1H), 4.94−5.00 (m, 2H), 4.85 (m, 1H), 4.40 (m, 1H), 4.20 (m, 1H), 3.60 (m, 1H), 3.14 (m, 1H), 3.04 (m, 4H), 2.96 (m, 2H), 2.79 (m, 2H), 1.62 (m, 2H), 1.53 (m, 2H),

1.38 (m, 4H) ppm. It displays absorption maxima at 400 nm and emission maxima at 556 nm in DMSO solution.

Preparation of 3-(11-Hydroxy-3,6,9-trioxa-1-undecoxy)thiophene (5). Compound **5** was prepared according to a modified procedure.[25] To a 100 mL three-necked round-bottom flask were added CuI (2.0 g, 10.5 mmol), potassium *t*-butoxide (*t*-BuOK) (8.9 g, 79.5 mmol), and tetraethylene glycol (51.5 g, 0.27 mol). When the mixture was stirred for 0.5 h, 3-bromothiophene (8.6 g, 52.8 mmol) was added via a syringe. The resulting mixture was stirred at 100 °C for 24 h, and then cooled down to room temperature. The solid was filtered and washed with CH_2C1_2. The combined organic solution was washed 10% HC1, 10% NH_4Cl, and NaCl solution successively, dried over anhydrous $MgSO_4$ and filtered. After removal of the solvent, the crude compound was purified by column chromatography on silica gel with EtOAc as a mobile phase to give the target compound (11 g, 75% yield) as light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11 (d, J = 5.2, 3.2 Hz, 1H), 6.72 (d, J = 5.2, 1.6 Hz, 1H), 6.21 (d, J = 3.2, 1.6 Hz, 1H), 4.06 (t, J = 5.2 Hz, 2H), 3.78 (t, J = 5.2 Hz, 2H), 3.61−3.67 (m, 10H), 3.54 (t, J = 4.4 Hz, 2H), 2.80 (s, 1H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ 157.76, 124.84, 119.76, 97.76, 72.72, 70.93, 70.84, 70.76, 70.52, 69.86, 69.76, 61.86 ppm.

Preparation of 3-(11-Bromo-3,6,9-trioxa-1-undecoxy)thiophene (6). Br_2 (2.75 g, 17.18 mmol) was added to a solution consisting of 15 mL of CH_3CN and triphenylphosphine (4.5 g, 17.17 mmol) under nitrogen gas at 0 °C. Compound **5** (4.66 g, 16.88 mmol) in CH_3CN (15 mL) was added dropwise to the mixed solution. When the mixture was stirred for 48 h at room temperature, the solvent was removed. The residue was dissolved in EtOAc and washed with saline solution. The organic layer was collected, dried over anhydrous $MgSO_4$, and concentrated at a reduced pressure. The residue was purified by column chromatography on silica using EtOAc as a mobile phase to give the target compound as a light brown oil (1.7 g, 30%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09 (d , J = 5.2 Hz, 3.2 Hz, 1H), 6.70 (d, J = 5.2 Hz, 1.6 Hz, 1H), 6.18 (d, J = 3.2 Hz, 1.6 Hz, 1H), 4.03 (t, J = 5.6 Hz, 2H), 3.62−3.72 (m, 4H), 3.58−3.61 (m, 8H), 3.39 (t, J = 5.6 Hz, 2H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ 157.78, 124.87, 119.76, 97.72, 71.35, 70.94, 70.85, 70.81, 70.68, 69.85, 69.77, 30.67 ppm.

Preparation of 2,5-Dibromo-3-(11-bromo-3,6,9-trioxa-1-undecoxy)thiophene (7). Freshly recrystallized *N*-bromosuccinimide (NBS) (0.44 g, 2.47 mmol) was added to the mixture consisting of THF (10 mL), acetic acid (10 mL), and compound **6** (0.4 g, 1.18 mmol). After the mixture was stirred for 1.5 h, it was poured into 100 mL of water and extracted with EtOAc (3 × 40 mL). The combined organic layer was further washed with saturated NaCl solution (3 × 50 mL), dried over anhydrous $MgSO_4$ and filtered. When the solvent was removed by rotary evaporation, the crude product was purified by column chromatography on silica gel with EtOAc as a mobile phase to give the product (0.41 g, 70% yield) as light brown oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.50 (s, 1H), 4.33 (t, J = 5.2 Hz, 2H), 3.94 (t, J = 4.8 Hz, 2H), 3.72−3.77 (m, 4H), 3.64−3.66 (m, 6H), 3.44 (t, J = 6.4 Hz, 2H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ 185.82, 179.62, 99.24, 73.99, 71.43, 71.40, 70.99, 70.87, 70.76, 68.92, 30.60 ppm.

Preparation of Poly[3-(11-bromo-3,6,9-trioxa-1-undecoxy)-thiophene] (Polymer 3). 2,5-Dibromo-3-(11-bromo-3,6,9-trioxa-1-undecoxy)thiophene (**7**) (2.75 g, 5.54 mmol) was added to a solution consisting of 30 mL of dried THF and CH_3MgBr (1.85 mL, 5.55 mmol). After the mixture was heated to reflux for 2 h, Ni(dppp)Cl_2 (20 mg, 0.04 mmol) was added, and the mixture was further stirred under reflux for 1 h. When the solvent was removed, the residue was dissolved in EtOAc, washed with saturated NaCl solution, and dried over anhydrous $MgSO_4$, filtered and concentrated at a reduced pressure. The dark brown residue was purified by flash column chromatography on silica gel eluting with EtOAc/CH_3OH (20:1, vol/vol), and further recrystallized using EtOAc/hexane to give 1.5 g of 98% head-to-tail coupled polymer **3** as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.72 (s, 1H), 4.23 (t, J = 4.4 Hz, 2H), 3.92 (t, J = 4.4 Hz, 2H), 3.78 (t, J = 6.2 Hz, 2H), 3.73 (m, 2H), 3.62−3.69 (m, 6H), 3.45 (t, J = 6.2 Hz, 2H) ppm. GPC (THF, polystyrene standard), M_n: 13 800 g/mol; polydispersity: 1.65. It displays absorption maxima at 376 nm and emission maxima at 474 nm in chloroform solution.

Preparation of Polymer 4a. Polymer **3** (0.2 g, 0.47 mmol), 1-thiolethyl-α-D-mannose tetraacetate (**3a**) (0.6 g, 1.47 mmol) and potassium carbonate (0.45 g, 3.27 mmol) were placed in a 50 mL round-bottom flask. THF (40 mL) was added and the mixture was stirred at room temperature for 48 h. After removal of the solvent, the residue was dissolved in methylene chloride (50 mL), washed with water three times, dried over anhydrous $MgSO_4$ and filtered. Upon removal of solvent by rotary evaporation, the residue was purified by flash column chromatography on silica gel with EtOAc/CH_3OH (5:1, vol/vol) as a mobile phase to give polymer **4a** (0.26 g, 86% yield) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.71 (s, 1H), 5.21−5.28 (m, 3H), 4.82 (s, 1H), 4.20−4.26 (m, 3H), 4.05−4.11 (m, 2H), 3.89−3.91 (m, 2H), 3.64−3.82 (m, 12H), 2.72−2.89 (m, 4H), 2.12 (s, 3H), 2.07 (s, 3H), 2.01 (s, 3H), 1.95 (s, 3H) ppm. It displays absorption maxima at 364 nm and emission maxima at 472 nm in chloroform solution.

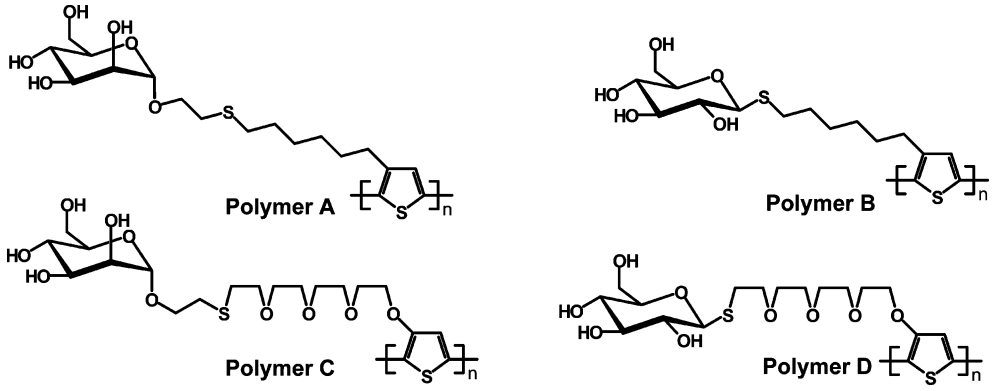
Preparation of Polymer 4b. Polymer **3** (0.2 g, 0.47 mmol), 1-thiol-β-D-glucose tetraacetrate (**3b**) (0.40 g, 1.09 mmol) and potassium carbonate (0.45 g, 3.27 mmol) were placed in a 50 mL round-bottom flask. THF (40 mL) was added and the mixture was stirred at room temperature for 48 h. When the solvent was removed, the residue was diluted with methylene chloride (50 mL), washed with water, dried over anhydrous $MgSO_4$, filtered, and concentrated at a reduced pressure. The crude product was purified by flash column chromatography on silica gel eluting with EtOAc/CH_3OH (5:1, vol/vol) to give the product (0.25 g, 88% yield) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.73 (s, 1H), 5.14−5.19 (m, 1H), 4.93−5.05 (m, 2H), 4.56 (m, 1H), 4.18−4.23 (m, 3H), 4.07−4.10 (m, 1H), 3.89 (m, 2H), 3.58−3.71 (m, 11H), 2.88−2.90 (m, 1H), 2.73−2.75 (m, 1H), 2.03 (s, 3H), 2.00 (s, 3H), 1.98 (s, 3H), 1.96 (s, 3H) ppm. It displays absorption maxima at 364 nm and emission maxima at 472 nm in chloroform solution.

Preparation of Polymer C. Solution of CH_3ONa (1 mL) was added to a solution consisting of dry CH_2Cl_2 (5 mL) and CH_3OH (10 mL), and polymer **4a** (0.2 g, 0.31 mmol). The reaction mixture was stirred at room temperature for 24 h. After rotary evaporation, the resulting residue was dissolved in 10 mL of water, dialyzed in a cellulose dialysis tube (cutoff 12 000) against water for 2 days (10 water changes), and lyophilized to give polymer **C** (0.13 g, 90%) as a light brown solid. ^{1}H NMR (400 MHz, D_2O): δ 5.20 (s), 4.63−4.75 (m), 4.14−4.20 (m), 4.02 (m), 3.57−3.81 (m), 2.58−2.87 (m) ppm. Polymer **C** is highly soluble in water, and displays absorption maxima at 350 nm and emission maxima at 460 nm in 0.1 M phosphate buffer (pH 7.2).

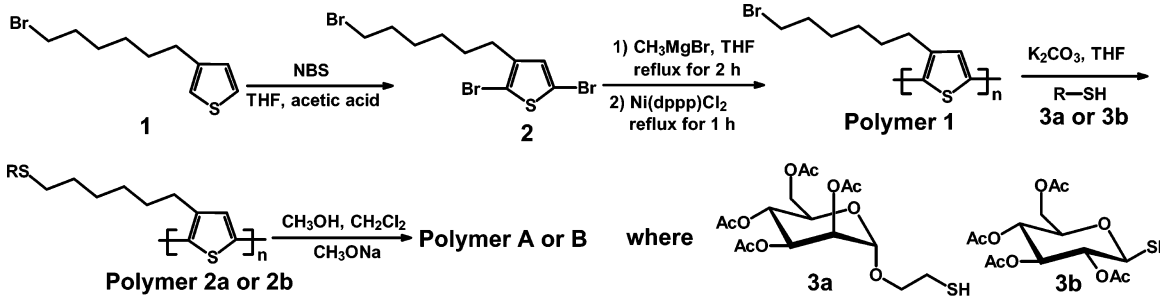
Preparation of Polymer D. A solution of CH_3ONa (1 mL) was added to a solution consisting of dry CH_2Cl_2 (5 mL) and CH_3OH (10 mL), and polymer **4b** (0.2 g, 0.33 mmol). The reaction mixture was stirred at room temperature for 24 h. After the solvent was removed by rotary evaporation, the resulting residue was dissolved in 10 mL of water, dialyzed in a cellulose dialysis tube (cutoff 12 000) against water for 2 days (10 water changes), and lyophilized to give the product (0.12 g, 84%) as a light brown solid. ^{1}H NMR (400 MHz, D_2O): δ 5.18 (s), 4.63 (m), 4.40−4.43 (m), 4.00−4.19 (m), 3.47−3.81 (m), 3.21−3.35 (m), 2.77−2.86 (m) ppm. Polymer **D** is highly soluble in water and displays absorption maxima at 352 nm and emission maxima at 460 nm in phosphate buffer (pH 7.2).

Preparation of 3-(11-Toluenesulfonyl-3,6,9-trioxa-1-undecoxy)thiophene (8). Toluenesulfonyl chloride (10 g, 52.7 mmol) was added to a mixture consisting of 50 mL of pyridine and 3-(11-hydroxy-3,6,9-trioxa-1-undecoxy)thiophene (**5**) (9.7 g, 35.15 mmol) in four portions at 0 °C. After the mixture was stirred for 13 h, it was poured into water, extracted with 100 mL of CH_2C1_2, and washed with 10% HCI. The combined organic layer was washed with 10% HC1, 10% NH_4Cl, and NaCl solution sequentially, and dried over anhydrous $MgSO_4$, filtered, and concentrated by rotary evaporation. The crude residue was purified by column chromatography on silica gel with CH_2Cl_2/EtOAc (5:1, vol/vol) as a mobile

Scheme 1. Chemical Structures of Regioregular Head-to-Tail Glycopolythiophenes Bearing α-D-Mannose or β-D-Glucose Residues



Scheme 2. Synthetic Route to Glycopolythiophenes (Polymers A and B)



phase to give the target compound (14 g, 93 yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8 Hz, 2H), 7.01 (d, J = 5.2, 3.2 Hz, 1H), 6.61 (d, J = 5.2, 1.4 Hz, 1H), 6.12 (d, J = 3.2, 1.4 Hz, 1H), 4.01 (t, J = 5.2 Hz, 2H), 3.96 (t, J = 4.8 Hz, 2H), 3.67 (t, J = 5.2 Hz, 2H), 3.46−3.55 (m, 6H), 2.27−3.41 (m, 4H), 2.27 (s, 3H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ 157.78, 145.00, 133.13, 130.06, 128.03, 124.86, 119.70, 97.69, 70.77, 70.71, 70.68, 70.59, 69.73, 69.61, 68.68, 21.69 ppm.

Preparation of 2,5-Dibromo-3-(11-toluenesulfonyl-3,6,9-trioxa-1-undecoxy)thiophene (9). Freshly recrystallized *N*-bromosuccinimide (NBS) (10 g, 56.2 mmol) was added to the mixture consisting of THF (40 mL), acetic acid (40 mL) and 3-(11-toluenesulfonyl-3,6,9-trioxa-1-undecoxy)thiophene (**8**) (10 g, 23.2 mmol). After the mixture was stirred for 1.5 h, it was added to 100 mL of water, and extracted with EtOAc (3 × 30 mL). The combined organic layer was washed with saturated NaCl solution (3 × 50 mL), dried over anhydrous $MgSO_4$ and filtered. When the solvent was removed, the crude product was purified by column chromatography on silica gel with CH_2Cl_2/EtOAc (10:1, vol/vol) to give monomer **9** (9.7 g, 71 yield) as a light orange oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8 Hz, 2H), 5.49 (s, 1H), 4.31 (t, J = 4.4 Hz, 2H), 4.08 (t, J = 4.4 Hz, 2H), 3.89 (t, J = 4.4 Hz, 2H), 3.67 (t, J = 4.4 Hz, 2H), 3.61 (t, J = 4.8 Hz, 2H), 3.58 (t, J = 4.4 Hz, 2H), 3.52 (m, 4H), 2.38 (s, 3H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ 185.75, 179.67, 145.09, 133.08, 130.09, 128.12, 99.22, 74.10, 71.28, 70.90, 70.71, 69.53, 68.86, 68.82, 44.74, 21.87 ppm.

Preparation of Poly[3-(11-bromo-3,6,9-trioxa-1-undecoxy)-thiophene] (polymer 3). To 2,5-dibromo-3-(11-toluenesulfonyl-3,6,9-trioxa-1-undecoxy)thiophene (**9**) (3.26 g, 5.54 mmol) was added 30 mL of dried THF and CH_3MgBr (1.85 mL, 5.55 mmol). After the mixture was heated to reflux for 2 h, Ni(dppp)Cl_2 (20 mg, 0.04 mmol) was added, and the mixture was stirred under reflux for another 1 h. When the solvent was removed, the residue was dissolved in EtOAc, washed with saturated NaCl solution and dried over anhydrous $MgSO_4$ and filtered. After removal of solvent by rotary evaporation, the dark brown residue was purified by flash column chromatography on silica gel with EtOAc/CH_3OH (20:1, vol/vol) as an eluent, and followed by recrystallization using EtOAc/hexane to give 1.5 g of 98% head-to-tail coupled polymer **3** as a yellow solid. The NMR data of polymer **3** obtained in this way is the almost same as that obtained by polymerization of bromide-bearing monomer **7**. GPC (THF, polystyrene standard), M_n: 13 300 g/mol; polydispersity: 1.71. It displays absorption maxima at 376 nm and emission maxima at 474 nm in chloroform solution.

Results and Discussion

We use a synthetic strategy of post-polymerization functionalization of bromide-bearing polythiophenes (polymers **1** and **3**) to prepare regioregular head-to-tail glycopolythiophenes since

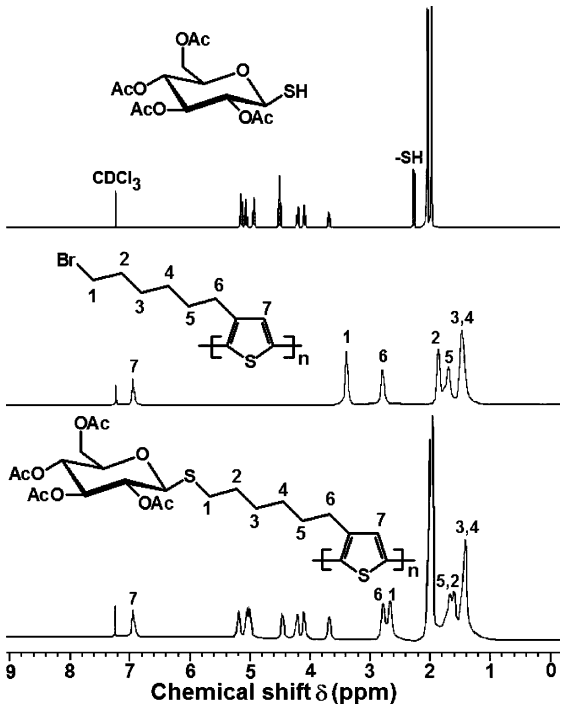


Figure 1. ^{1}H NMR spectra of 1-thiol-β-D-glucose tetraacetrate (**3b**), poly(3-bromohexylthiophene) (polymer **1**), and glycopolythiophene bearing β-D-glucose-tetraacetrate residues (polymer **2b**) in $CDCl_3$ solution.

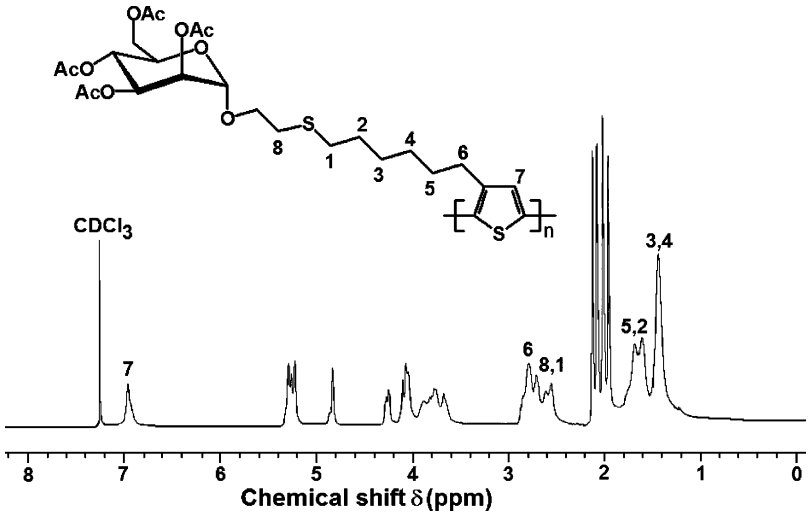


Figure 2. ^{1}H NMR spectra of glycopolythiophene bearing α-D-mannose-tetraacetate residues (polymer **2a**) in $CDCl_3$ solution.

the polymerization for regioregular head-to-tail polythiophenes is typically achieved by Grignard metathesis method initially reported by McCullough et al.[23,26−29] Regioregular head-to-tail poly(3-bromohexylthiophene) (polymer **1**) was synthesized via condensation polymerization using the Grignard metathesis method in excellent yield and with a high degree of polymerization (Scheme 2),[23] according to gel permeation chromatography (yield 90%, M_n: 25 900 g/mol; polydispersity: 1.75 gel permeation chromatography). It is readily soluble in common organic solvents such as tetrahydrofuran (THF) and chloroform. Glucose or mannose tetraacetrate residues were introduced to regioregular head-to-tail polythiophene by treating polymer **1** with 1-thiolethyl-α-D-mannose tetraacetate (**3a**) or 1-thiol-β-D-glucose tetraacetrate (**3b**) in THF solution in a basic condition at room temperature via thioether formation (Scheme 2). Figure 1 shows ^{1}H NMR spectra of 1-thiol-β-D-glucose tetraacetrate (**3b**), poly(3-bromohexylthiophene) and glycopolythiophene bearing β-D-glucose-tetraacetrate residues (polymer **2b**). ^{1}H NMR spectra of polymer **1** show that methylene groups adjacent to bromide atoms in polymer **1** display the signal peaks around 3.41 ppm (Figure 1). Treatment of polymer **1** with 1-thiol-β-D-glucose tetraacetate caused the signal peaks corresponding to these methylene groups shift to the higher field region around 2.66 ppm (Figure 1), indicating complete formation of thioether linkage in polymer **2b** while the signal peaks around 2.81 ppm corresponding to methylene groups adjacent to thiophene backbone in the polymer **1** shift slightly to the higher field around 2.78 ppm as they are far from the thioether bond in polymer **2b**. Moreover, the signal peaks around 1.87 ppm corresponding to methylene groups at 2 position in polymer **1** shift to the higher field region around 1.61 ppm in polymer **2b** (Figure 1). The similar chemical shifts were also found in glycopolythiophene bearing α-D-mannose-tetraacetrate residues (polymer **2a**) (Figure 2). These results indicate that this post-polymerization functionalization method can offer a general, fast and efficient approach to quantitatively introduce a variety of carbohydrate residues to conjugated polythiophenes via thioether bridges. Glycopolythiophenes bearing α-D-mannose and β-D-glucose residues (polymers **A** and **B**) were prepared by sequentially deacetylating polymers **2a** and **2b** under Zemplén conditions in methanol and methylene chloride containing sodium methoxide at room temperature, respectively (Scheme 2).

The solubility of the glycopolymers is different from its precursor polymer. The precursor polymer **1** is readily soluble

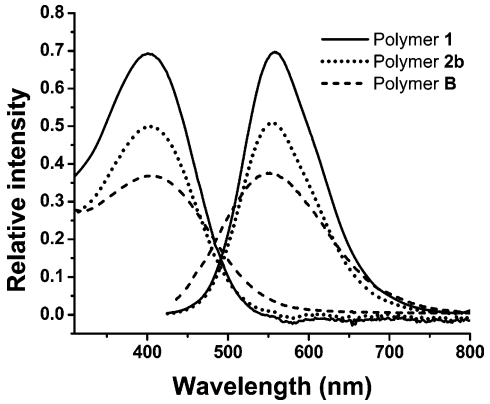


Figure 3. UV−visible absorption and fluorescent spectra of polymers **1** and **2b** $CHCl_3$, and polymer **B** in DMSO solution.

in common solvents such as THF, chloroform and methylene chloride, and moderately soluble in DMF and DMSO, but insoluble in ethanol, methanol, acetone and water. Polymers **2a** and **2b** are readily soluble in common solvents such as THF, chloroform, methylene chloride, DMF and DMSO. Polymers **A** and **B** are soluble in DMF and DMSO, but completely insoluble in water because of the hydrophobic feature of hexyl tethered spacers between carbohydrates and the polymer backbone.

The precursor polymer **1** exhibits UV−visible absorption maximum peak at 400 nm, and emission maximum peak at 558 nm in chloroform solution, which were ascribed to the $\pi-\pi^*$ transition of the conjugated polymer backbone (Figure 3). Polymer **2a** or **2b** bearing peracetylated β-D-glucose or α-D-mannose residues displays UV−Visible absorption maximum peak at 400 nm, and emission maximum peak at 556 nm in chloroform solution, which are almost similar to those of the precursor polymer **1** in chloroform solution. Polymers **A** and **B** show UV−visible absorption maximum peak at 404 nm, and emission maximum peak at 552 nm in DMSO solution.

In order to prepare water-soluble glycopolythiophenes, we used hydrophilic oligo(ethylene glycol) as tethered spacers between carbohydrate residues and the polymer backbone. To covalently attach carbohydrates to polythiophene backbone through tetra(ethylene glycol) tethers, we developed a synthetic strategy based on the use of 2,5-dibromo-3-(11-bromo-3,6,9-trioxa-1-undecoxy)thiophene (**7**), which was obtained by bromination of 3-(11-hydroxy-3,6,9-trioxa-1-undecoxy)thiophene (**5**) in acetonitrile solution containing bromine and triph-

Scheme 3. Synthetic Route to Water-Soluble Regioregular Head-to-Tail Glycopolythiophenes (Polymers C and D)

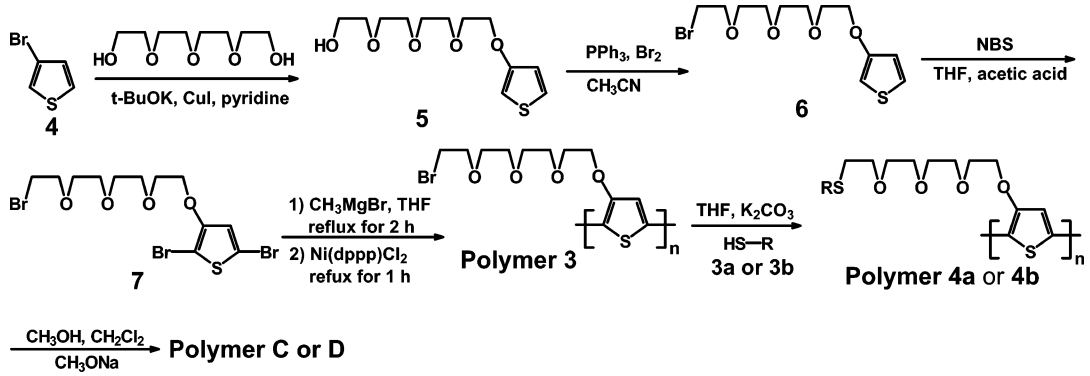


Table 1. Fluorescent Quantum Yields of Polythiophenes

polymer	**1**	**2b**	**B**	**3**	**4a**	**4b**	**C**	**D**
fluorescent quantum yield	2%	3%	2%	0.4%	0.5%	0.4%	0.8%	0.7%
solvent	$CHCl_3$	$CHCl_3$	DMSO	$CHCl_3$	$CHCl_3$	$CHCl_3$	phosphate buffer (pH 7.2)	phosphate buffer (pH 7.2)

enylphosphine affording 3-(11-bromo-3,6,9-trioxa-1-undecoxy)-thiophene (**6**), and sequential bromination of intermediate **6** in a solution of THF and acetic acid in the presence of *N*-bromosuccinimide (NBS) (Scheme 3). Regioregular head-to-tail poly[3-(11-bromo-3,6,9-trioxa-1-undecoxy)thiophene] (polymer **3**), a bromide-bearing polythiophene with tetra(ethylene glycol) tethered spacers, were prepared by condensation polymerization of monomer **7** using the Grignard metathesis method (Scheme 3). ^{1}H NMR spectra of 2,5-dibromo-3-(11-bromo-3,6,9-trioxa-1-undecoxy)thiophene (**7**) show that thiophene moiety exhibits the signal peak around 5.50 ppm while methylene group adjacent to thiophene moiety displays the signal peak around 4.33 ppm (Figure 4). After polymerization, the signal peak corresponding to the thiophene moiety in polymer **3** shifts to lower field region around 5.72 ppm while the signal peak corresponding to these methylene groups adjacent to the polythiophene backbone shift to higher field region around 4.23 ppm (Figure 4). In addition, bromide-bearing polymer **3** was also prepared by condensation polymerization of 2,5-dibromo-3-(11-toluenesulfonyl-3,6,9-trioxa-1-undecoxy)-thiophene (**9**) using the Grignard metathesis method. During the polymerization, good leaving toslate groups were replaced by bromide groups released by Grignard metathesis reaction (Scheme 4). Monomer **9** were prepared by tosylation of 3-(11-hydroxy-3,6,9-trioxa-1-undecoxy)thiophene (**5**) affording 3-(11-toluenesulfonyl-3,6,9-trioxa-1-undecoxy)thiophene (**8**), and sequential bromination of the intermediate **8** in a solution of THF and acetic acid in the presence of *N*-bromosuccinimide (NBS) (Scheme 4). β-D-Glucose and α-D-mannose residues were conjugated to regioregular head-to-tail polythiophene by treating polymer **3** with 1-thiolethyl-α-D-mannose tetraacetate (**3a**) and 1-thiol-β-D-glucose tetraacetrate (**3b**) in THF solution with a basic condition at room temperature via thioether formation, respectively, affording polymers **4a** and **4b**, and followed by sequentially deacetylation of polymers **4a** and **4b** under Zemplén

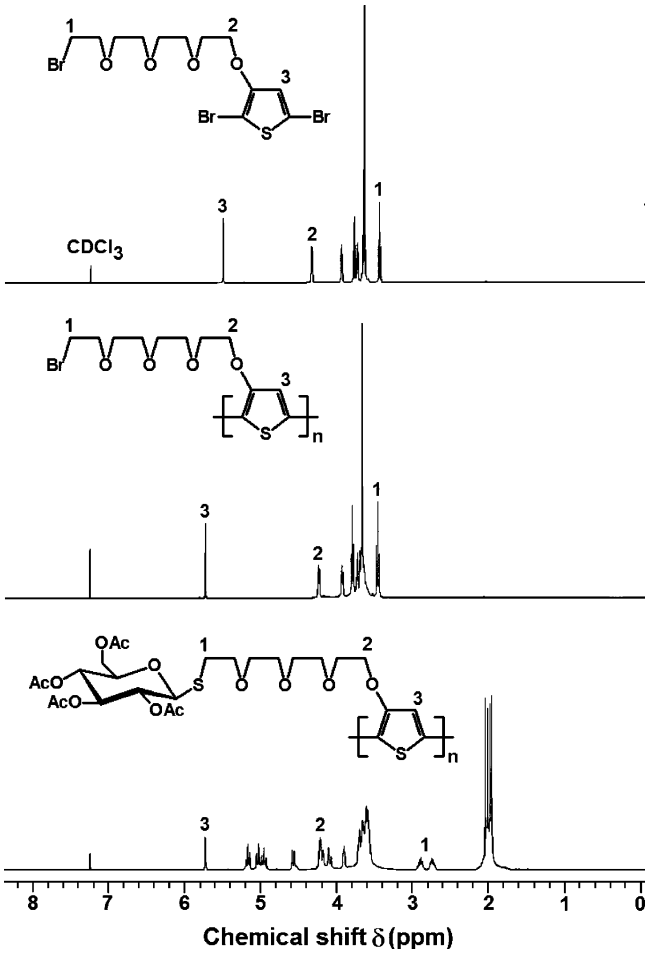


Figure 4. ^{1}H NMR spectra of 2,5-dibromo-3-(11-bromo-3,6,9-trioxa-1-undecoxy)thiophene (**7**), poly[3-(11-bromo-3,6,9-trioxa-1-undecoxy)-thiophene] (polymer **3**), and glycopolythiophene bearing β-D-glucose-tetraacetrate residues (polymer **4a**) in $CDCl_3$ solution.

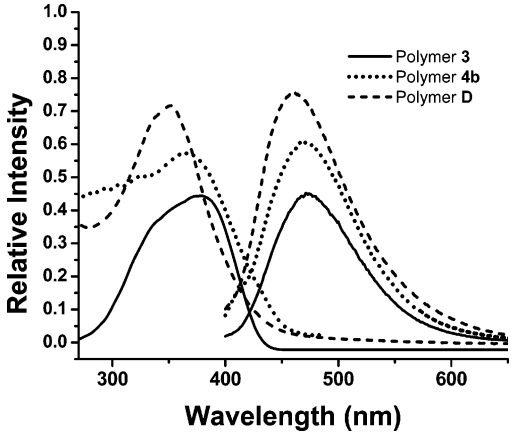
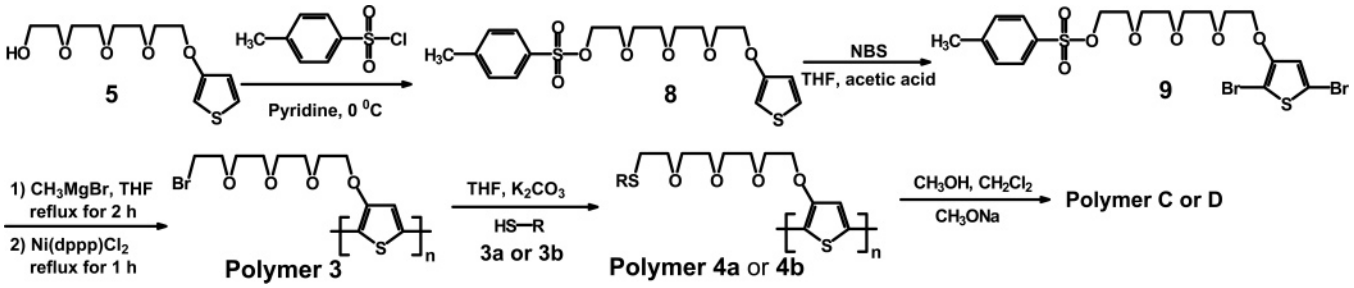


Figure 5. UV−visible absorption and fluorescent spectra of polymers **3** and **4a** in $CHCl_3$ solution and polymer **D** in 0.1 M phosphate buffer solution.

Scheme 4. Alternative Synthetic Route to Water-Soluble Regioregular Head-to-Tail Glycopolythiophenes (Polymers C and D)



conditions in a solution of methanol and methylene chloride containing sodium methoxide at room temperature, affording polymers **C** and **D** (Schemes 3 and 4). This approach renders conjugated glycopolymers highly soluble in water. ^{1}H NMR spectra of polymer **3** show that methylene groups adjacent to bromide atoms in polymer **3** display the signal peaks around 3.45 ppm (Figure 4). Treatment of polymer **3** with 1-thiol-β-D-glucose tetraacetate caused the signal peaks corresponding to these methylene groups shift to the higher field region around 2.89 and 2.74 ppm, indicating complete formation of thioether linkage in polymer **4b** (Figure 4).

Precursor polymer **3** shows UV−visible absorption maxima at 376 nm and emission maxima at 474 nm in chloroform solution (Figure 5). Polymers **4a** and **4b** display UV−visible absorption maxima at 364 nm and emission maxima at 472 nm in chloroform solution. Polymers **C** and **D** exhibit UV−visible absorption maxima at 350 nm and emission maxima at 460 nm in 0.1 M phosphate buffer (pH 7.2). All polythiophenes display low fluorescence with fluorescent quantum yield ranging from 0.4% to 3% which were determined by using quinine sulfate in 0.1 N sulfuric acid as the reference for absolute quantum efficiency ($\phi_n = 55\%$).[22] Precursor polymer **3** with tetra(ethylene glycol) tethered spacers displays lower fluorescence intensity than precursor polymer **1** (Table 1). Polymers **A** and **B** in DMSO solution possess the same fluorescent quantum yield with their precursor polymer **1** in chloroform. However, glycopolythiophenes (polymers **C** and **D**) in 0.1 M phosphate buffer (pH 7.2) exhibit a little higher fluorescent intensity than their precursor polymer **3** in chloroform solution (Table 1).

In order to assess the capability of highly water-soluble conjugated glycopolythiophenes, Concanavalin A (Con A), a member of the lectin family, was chosen as a target protein since it is a well-know α-mannose- and α-glucose-binding protein and exists predominantly as a tetramer of four identical subunits approximately 26 000 Da at neutral and alkaline pH levels.[30] It has four binding sites and can interact with four α-mannose or α-glucose units simultaneously. Below pH 5.6, however, it dissociates into active dimers. It binds two metal ions per monomer; a transition metal, Mn^{2+} and Ca^{2+}, must be present for saccharide binding.[30] Titration of Con A into a phosphate buffer (pH 7.2) containing β-glucose-bearing polymer **D** shows no significant change of the polymer fluorescence (Figure 6). This is consistent with a literature report that Con A displays no binding ability to β-glucose.[31] This result indicates that there are not any nonspecific interactions between the glycopolythiophene and Con A. However, titration of Con A into a phosphate buffer (pH 7.2) containing α-mannose-bearing polymer **C** causes a concentration-dependent quenching of the polymer fluorescence (Figure 7) and a very small decrease of the polymer UV−visible absorption, clearly indicating that the α-mannose-bearing polymer **C** specifically binds to Con A, resulting in quenching of the polymer fluorescence.

Conjugated polymers feature short emissive lifetimes on the order of 0.2−0.5 ns unless they possess organometallic fragments.[32−34] As a result, only static quenching is predominant.[32−34] In static quenching, the quencher forms a ground-state complex with the fluorophore, once generated, the excited-state is immediately and quantitatively quenched after excitation. Quenching constant (K_{SV}) in static quenching equals the apparent complex formation constant of quencher to fluorophore. Using the Stern−Volmer relationship provides a simple way to determine binding constants.[35] A quantitative measure of the

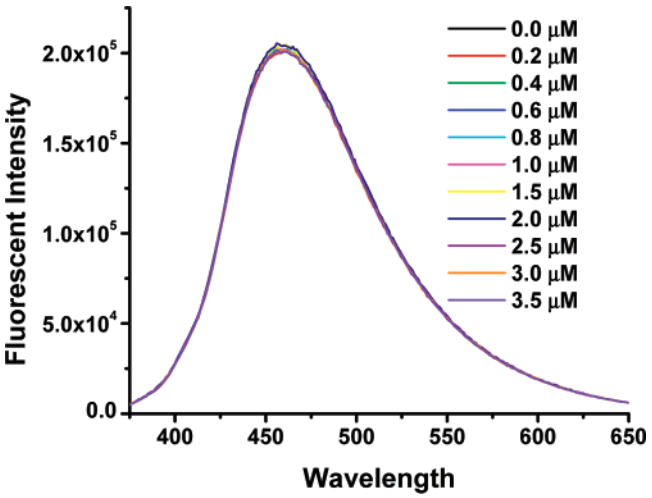


Figure 6. Fluorescent spectra of 1.0×10^{-6} M β-glucose-bearing polymer **D** in the absence and presence of different concentrations of Con A in 0.1 M phosphate buffer (pH 7.2) containing 0.1 mM $CaCl_2$ and 0.1 mM $MnCl_2$.

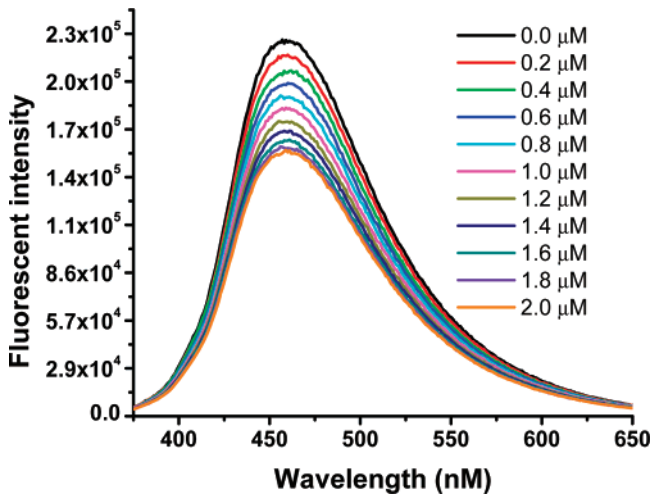


Figure 7. Fluorescent spectra of 1.0×10^{-6} M α-mannose-bearing polymer **C** in the absence and presence of different concentrations of Con A in 0.1 M phosphate buffer solution (pH 7.2) containing 0.1 mM $CaCl_2$ and 0.1 mM $MnCl_2$.

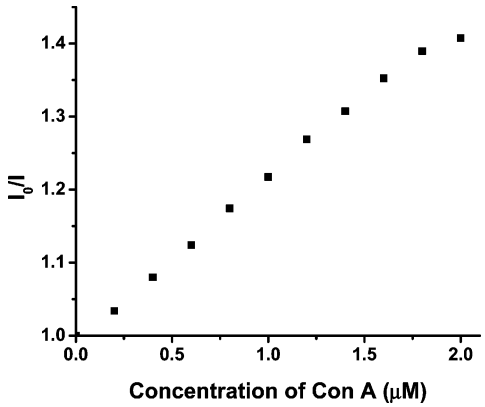


Figure 8. Stern−Volmer curve of 1.0×10^{-6} M α-mannose-bearing polymer **C** with different Con A concentrations in phosphate buffer (pH 7.2) containing 0.1 mM $CaCl_2$ and 0.1 mM $MnCl_2$.

fluorescence quenching can be achieved by determining the well-known Stern−Volmer constant, K_{SV}:[35]

$$I_0/I = 1 + K_{SV}[Q]$$

where I_0 is the fluorescent intensity in the absence of quencher and I is the fluorescent intensity as a function of quencher concentration [Q]. The equation reveals that I_0/I increases in direct proportion to the quencher concentration, and K_{SV} is the Stern−Volmer constant, defining the efficiency of quenching. When all other variables are held constant, the higher the K_{SV}, the lower the concentration of quencher required to quench the fluorescence.[35] The Stern−Volmer quenching constant of polymer **C** by Con A was calculated as 2.15×10^5 (Figure 8). This large binding constant of is achieved by multivalent interactions of α-mannose-bearing glycopolythiophene with Con A.

Conclusion

In conclusion, we have applied a facile, versatile post-polymerization functionalization approach to attach monosaccharides to regioregular head-to-tail polythiophenes based on the reaction of thiols with bromide groups in precursor polymers to form thioether bridges for well-defined regioregular head-to-tail glycopolythiophenes.[16,17] The water solubility of glycopolythiophenes have been achieved by using hydrophilic tetrakis(ethylene glycol) tethered spacers between the polymer backbone and carbohydrate residues. α-Mannose-bearing glycopolythiophene displays specific binding to Con A through multivalent cooperative interactions with binding constant of 2.15×10^5. We believe that this approach offers a very efficient and fast method to synthesize well-defined fluorescent conjugated glycopolymers bearing a variety of carbohydrate pendants for potential biosensing applications for cells and viruses as it should work equally well with any thiol-functionalized monosaccharide, disaccharide and oligosaccharides.

Acknowledgment. We acknowledge the Research Excellence Fund of Michigan Tech and United States Department of Agriculture (contract number: 2007-35603-17740) through National Research Initiative Competitive Grants Program for support of the work.

Supporting Information Available: Figures showing the ^{1}H NMR and ^{13}C NMR spectra of 3-(11-hydroxy-3,6,9-trioxa-1-undecoxy)thiophene (**5**), 3-(11-bromo-3,6,9-trioxa-1-undecoxy)-thiophene (**6**), 5-dibromo-3-(11-bromo-3,6,9-trioxa-1-undecoxy)-thiophene (**7**), 3-(11-toluenesulfonyl-3,6,9-trioxa-1-undecoxy)thiophene (**8**), and 2,5-dibromo-3-(11-toluenesulfonyl-3,6,9-trioxa-1-undecoxy)thiophene (**9**). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Lis, H.; Sharon, N. *Chem. Rev.* **1998**, *98*, 637−674.
(2) Mammen, M.; Choi, S. K.; Whitesides, G. M. *Angew. Chem., Int. Ed.* **1998**, *37*, 2755−2794.
(3) Jelinek, R.; Kolusheva, S. *Chem. Rev.* **2004**, *104*, 5987−6015.
(4) Sears, P.; Wong, C. H. *Science* **2001**, *291*, 2344−2350.
(5) Juan, Z.; Swager, T. M.; Poly(arylene ethynylene)s in chemosensing and biosensing. In *Advances in Polymer Science*; Springer-Verlag Berlin: Berlin, 2005; Vol. 177, pp 151−179.
(6) Bunz, U. H. F. *Chem. Rev.* **2000**, *100*, 1605−1644.
(7) McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2537−2574.
(8) Liu, B.; Bazan, G. C. *Chem. Mater.* **2004**, *16*, 4467−4476.
(9) Pinto, M. R.; Schanze, K. S. *Synthesis-Stuttgart* **2002**, 1293−1309.
(10) Thomas, S. W.; Joly, G. D.; Swager, T. M. *Chem. Rev.* **2007**, *107*, 1339−1386.
(11) Kim, I. B.; Wilson, J. N.; Bunz, U. H. F. *Chem. Commun.* **2005**, 1273−1275.
(12) Disney, M. D.; Zheng, J.; Swager, T. M.; Seeberger, P. H. *J. Am. Chem. Soc.* **2004**, *126*, 13343−13346.
(13) Baek, M. G.; Stevens, R. C.; Charych, D. H. *Bioconjugate Chem.* **2000**, *11*, 777−788.
(14) Kim, I. B.; Erdogan, B.; Wilson, J. N.; Bunz, U. H. F. *Chem.—Eur. J.* **2004**, *10*, 6247−6254.
(15) Kim; I.-B.; Dunkhorst; A.; Bunz; F.; U. H. *Langmuir* **2005**, *21*, 7985−7989.
(16) Xue, C. H.; Donuru, V. R. R.; Liu, H. Y. *Macromolecules* **2006**, *39*, 5747−5752.
(17) Xue, C. H.; Jog, S. P.; Murthy, P.; Liu, H. Y. *Biomacromolecules* **2006**, *7*, 2470−2474.
(18) Li, C.; Numata, M.; Takeuchi, M.; Shinkai, S. *Angew. Chem., Int. Ed.* **2005**, *44*, 6371−6374.
(19) Karlsson, K. F.; Asberg, P.; Nilsson, K. P. R.; Inganas, O. *Chem. Mater.* **2005**, *17*, 4204−4211.
(20) Ho, H. A.; Dore, K.; Boissinot, M.; Bergeron, M. G.; Tanguay, R. M.; Boudreau, D.; Leclerc, M. *J. Am. Chem. Soc.* **2005**, *127*, 12673−12676.
(21) Le Floch, F.; Ho, H. A.; Harding-Lepage, P.; Bedard, M.; Neagu-Plesu, R.; Leclerc, M. *Adv. Mater.* **2005**, *17*, 1251−1254.
(22) Demasa, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991−1024.
(23) Zhai, L.; Pilston, R. L.; Zaiger, K. L.; Stokes, K. K.; McCullough, R. D. *Macromolecules* **2003**, *36*, 61−64.
(24) Africa; G. B.; Juan; G. L.; Joaquin.; I. G.; Fernando; O. C.; Clara; U.; Antonio; V. B.; Francisco, S. G. *Synthesis* **2001**, 1057−1064.
(25) Marsella, M. J.; Carroll, P. J.; Swager, T. M. *J. Am. Chem. Soc.* **1995**, *117*, 9832−9841.
(26) Jeffries-El, M.; Sauve, G.; McCullough, R. D. *Macromolecules* **2005**, *38*, 10346−10352.
(27) Jeffries-El, M.; Sauve, G.; McCullough, R. D. *Adv. Mater.* **2004**, *16*, 1017-+.
(28) Loewe, R. S.; Ewbank, P. C.; Liu, J. S.; Zhai, L.; McCullough, R. D. *Macromolecules* **2001**, *34*, 4324−4333.
(29) Bjornholm, T.; Hassenkam, T.; Greve, D. R.; McCullough, R. D.; Jayaraman, M.; Savoy, S. M.; Jones, C. E.; McDevitt, J. T. *Adv. Mater.* **1999**, *11*, 1218−1221.
(30) Simanek, E. E.; McGarvey, G. J.; Jablonowski, J. A.; Wong, C. H. *Chem. Rev.* **1998**, *98*, 833−862.
(31) Park, S.; Lee, M. R.; Pyo, S. J.; Shin, I. *J. Am. Chem. Soc.* **2004**, *126*, 4812−4819.
(32) Tan, C. Y.; Alas, E.; Muller, J. G.; Pinto, M. R.; Kleiman, V. D.; Schanze, K. S. *J. Am. Chem. Soc.* **2004**, *126*, 13685−13694.
(33) Zhou, Q.; Swager, T. M. *J. Am. Chem. Soc.* **1995**, *117*, 12593−12602.
(34) Liu, M.; Kaur, P.; Waldeck, D. H.; Xue, C. H.; Liu, H. Y. *Langmuir* **2005**, *21*, 1687−1690.
(35) Lakowicz, R.; J. *Principles of Fluorescence Spectroscopy*; Plenum Press: New York, 1986.

MA070927K