Macromolecules **2009**, *42*, 921−926

Fiber-Optic Detection of Explosives Using Readily Available Fluorescent Polymers

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Received November 3, 2008; Revised Manuscript Received January 10, 2009

ABSTRACT: A series of simple fluorescent polymers were readily synthesized by palladium-catalyzed Suzuki coupling reactions of dibromoterephthalates containing the small methyl and large cholesteryl esters with bisboronic esters derived from alkylated fluorene and *N*-hexyldiphenylamine. The polymers had an inherent viscosity ranging from 0.25 to 0.74 dL/g and were characterized by spectroscopic methods. The glass transition temperatures for these polymers ranged from 90 to 104 °C, and the decomposition temperatures were in a range of 291−435 °C in nitrogen. All the polymers emit around 450−530 nm with the absolute fluorescence quantum efficiencies up to 61%. The polymers were tested for detection of the vapor of explosive analyte (2,4-dinitrotoluene) as a thin film coated on glass substrate and on optic-fiber tips. Explosive detection using the polymer-coated optic-fiber probe has been demonstrated to be fast and sensitive, with the fluorescence quenching efficiency reaching 48% within 25 s or 61% within the first minute.

Introduction

At present, there is a growing demand for various types of chemosensors for applications in homeland security,[1] forensic analysis,[2] and land-mine detection.[3] Some spectroscopic methods for explosive detection are currently available, such as ion mobility spectrometry,[4] gas chromatography coupled with mass spectrometry,[5,6] and surface-enhanced Raman spectroscopy.[7] These detection methods require instrumentation that are either too big, expensive, and needed to be calibrated frequently or too sophisticated to handle for on-field testing.[8] Recently, conjugated polymers have received a tremendous deal of attention as fluorescence-based chemosensors due to sensing enhancements associated with electronic communication between receptors along the polymer backbone.[9,10] The vast majority of the detection methods utilize the "turn-off" effect in the presence of analyte rather than the fluorescence "turn-on" effect.[11−17] In 1998, Swager and co-workers used the fluorescence quenching transduction mechanism together with the amplifying nature of conjugated polymers to design a pentiptycene containing polymer for sensing nitroaromatic compounds (NACs).[18] The rigid pentiptycene group is an important design feature, which prevents the polymer chains from strongly aggregating and the emission from self-quenching in the solid state and thus allows for multidimensional exciton transport and higher amplification that is critical for trace detection of explosives.[19]

Utilizing sensory polymer films coated on a large substrate (e.g., glass plate) has become the common method of choice for explosive detection.[20] However, several factors could limit the scope of this method in certain applications. Thicker film can generate a high fluorescence level due to the unquenched under layer that does not interact with explosive vapors, adversely affecting observation of the quenching effect, while thinner film tends to absorb only a limited amount of excitation light power, thus giving a low fluorescence level. The polymers also tend to degrade over time due to photo-oxidation when using a high excitation power. Strong excitation could also cause continuous drop in signal level that could produce false quenching effect. Another issue is the instrumentation. Use of a conventional or custom-made fluorescence spectrum analyzer is conceivable but not practical for some applications such as remote and stealth sensing because the sensing probe (e.g., sensory polymer coated glass substrate) or the explosive analyte must be close to the instrument. One alternative method is to use a fiber-optic probe for explosive detection. In principle, a two-fiber probe configuration can be envisioned. A sensory polymer film is coated on the end of very small but long optic fibers, and the excitation can be delivered through the fiber. At the same time, the fluorescent signal can be collected through another fiber that is in a close contact with the other fiber. The spectrum or data analyzer can be far away from the multiple explosive sensing probes that could be placed in nearly any places, making this detection system portable, stealth, and capable of remotely accessing hard-to-reach areas. A fiber-optic system for explosive detection is thus deemed to be low-cost, flexible, and lightweight, with extremely low optical loss over long transmission distances.

Regarding the sensory polymers, they should be readily available or easy to make, structurally simple for variation and modification, and highly fluorescent. The polymers should also be sensitive to a trace amount of target analyte or NACs and result in a large drop in fluorescence intensity within a short period of time upon exposure to the analyte vapor. With these basic requirements in mind, we have designed two series of fluorescence "turn-off" polymers (**4a,b** and **5a,b**, Scheme 1) for the fiber-optic detection of NACs such as 2,4,6-trinitrotoluene (TNT). These polymers can be readily synthesized by the Suzuki cross-coupling reaction of dibromide and bisboronic acid ester monomers. For the dibromide monomers, we chose dibromoterephthalates **1a,b** (Scheme 1), as they are readily available and can be structurally modified at the ester groups,

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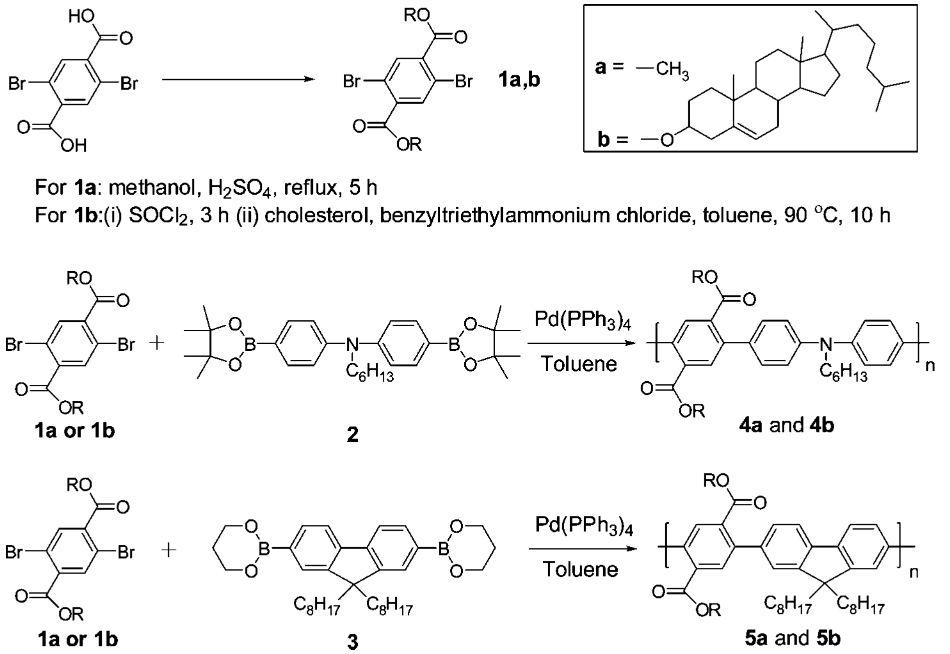
10.1021/ma802460q CCC: $40.75 © 2009 American Chemical Society
Published on Web 02/03/2009

Scheme 1. Synthetic Routes to Monomers 1a,b and Polymers 4a,b−5a,b



such as a small methyl and large cholesteryl ester in this case. Among two bisboronic ester monomers (**2** and **3**, Scheme 1), monomer **3** is commercially available. The bulky cholesterol esters in monomer **1b** and long alkyl chains in monomer **3** are expected to act as a site-isolating group to prevent the interchain interaction and create large free volume in the resulting polymers, which therefore should enhance the fluorescence quantum efficiency and help to trap the analyte molecules, respectively. Monomer **2** is designed to have an electron-donating diphenylamine moiety, in order to probe any donor−acceptor interaction with the electron-accepting NACs, thus enhancing the detection sensitivity. Herein we report the synthesis, characterization, and sensing properties of four new polymers. The sensing experiments are done with the polymer films coated on glass substrate and on the optic-fiber tips.

Experimental Section

Materials. 9,9-Dioctylfluorene-2,7-bis(trimethyleneborate) (**3**) was purchased from Aldrich and used without purification. 2,5-Dibromoterephthalic acid was purchased from Aldrich Chemicals Inc. All the solvents and reagents were purchased from Aldrich Canada Inc. and used without further purification. Macherey-Nagel precoated TLC plates (silica gel 60 G/UV$_{254}$, 0.25 mm) were used for thin-layer chromatography (TLC) analysis. Silica gel (Silicycle Chemical Division, 0.04−0.06 mm, 230−400 mesh) was used as the stationary phase for column chromatography.

Measurements. Infrared measurements of thin films of polymers cast on the NaCl salt plates were performed on a Varian 1000 FT-IR Scirnitar. ^{1}H NMR and ^{13}C NMR were measured by a Bruker Advanced Digital NMR 300 spectrophotometer. The UV absorption of the compounds was recorded using a UV−vis Lambda 900 spectrophotometer while the photoluminescence of products were measured by a Shimadzu RF-1501 spectrofluorophotometer. Absolute luminescence quantum efficiencies of polymer films were measured by using an integral sphere at the Changchun Institute of Applied Chemistry, China. Mass spectrometry was done with the Micromass Quattro LC ESI at the University of Ottawa. Decomposition temperatures of products were measured on a thermogravimetric analyzer (TGA) TGA 2950 CE instrument at a heating rate of 20 °C/min. Glass transition temperatures (T_g) of all the polymers were recorded by differential scanning calorimetry (DSC) on a DSC Q100 instrument at a heating rate of 10 °C/min under nitrogen. The apparent molecular weights of selected polymers were determined by gel permeation chromatography (GPC) relative to polystyrene standards using chloroform at ambient temperature at a flow rate of 1.0 mL/min; a UV detector set at 254 nm wavelength was used for detection. Inherent viscosities were measured in chloroform solution at 30 °C using an Ubbelohde dilution viscometer.

Syntheses. *4,4′-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)-N-hexyldiphenylamine (**2**).* **2** was prepared as reported before.[22]

*Dimethyl 2,5-Dibromoterephthalate (**1a**).* Concentrated H_2SO_4 (1 mL) was added to a mixture of 2,5-dibromoterephthalic acid (7.00 g, 21.6 mmol) and methanol (80 mL), and then the reaction mixture was refluxed for 8 h. After cooling to room temperature, the white precipitated was collected by filtration and then recrystallized from dicholoromethan/methanol to afford **1a** in 90% yield (6.90 g); mp 140 °C (DSC). ^{1}H NMR (300 MHz, DMSO-d_6): δ_H 8.08 (s, 2 H), 3.87 (s, 6 H). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C 164.25, 135.95, 135.26, 118.95, 53.00.

*Diester−Dibromide **1b**.* A mixture of 2,5-dibromoterephthalic acid (1.00 g, 3.09 mmol) and thionyl chloride (10 mL) was heated to reflux for at least 3 h. Thionyl chloride was rotor-evaporated to give 2,5-dibromoterephthaloyl dichloride. Under argon, to a solution of cholesterol (2.30 g, 6 mmol) and 2,5-dibromoterephthalaoyl dichloride (0.50 g, 1.4 mmol) in dry toluene (40 mL), benzyltriethylammonium chloride (0.25 g, 10 mol %) was added. The mixture was heated at 90 °C for at least 10 h. After cooling to room temperature, ethyl acetate was added to precipitate out the product. The collected crude product was dissolved in chloroform, filtered to remove residues, and purified by column chromatography (chloroform/hexane, 2:1.5 v/v). The product **1b** was obtained as white solids (0.90 g, 62%); mp 259−261 °C. MS (*m*/*z*): 1621, 1060. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 8.00 (s, 2H), 5.46 (s, 2H), 4.91 (m, 2H), 2.52 (d, 4H), 2.03−0.72 (m, 82H). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 163.77, 139.22, 136.25, 136.03, 123.19, 119.97, 56.68, 56.13, 50.01, 45.80, 42.32, 39.71, 39.52, 37.97, 36.96, 36.63, 36.19, 35.81, 31.93, 31.85, 28.24, 28.03, 27.72, 24.30, 23.84, 22.84, 22.58, 21.06, 19.36, 18.73, 11.87, 8.63.

General Procedure for Polymerization. In a 25 mL, two-necked round-bottomed flask equipped with a condenser and an argon purge line, dibromo monomer (1.0 mmol), diboronic acid monomer (1.0 mmol), and terakis(triphenylphosphine)palladium(0) (0.5 mol %) were placed and stirred under argon for few minutes. To this mixture, the argon-purged toluene (20% of concentration)

Table 1. Characterization and Relevant Photophysical Data for Polymers 4a,b−5a,b

	η_{inh} (dL/g)[a]	M_w (10^{-4})[b]	PDI[b]	T_g (°C)[c]	T_d (°C)[d]	Abs λ_{max} (nm)[e]	PL λ_{max} (nm) solution[f]	PL λ_{max} (nm) film[g]	Φ_F[h]
4a	0.36	1.74	3.12	97	367	333, 381	543	532	0.07
4b	0.25	2.46	2.07	100	291	329, 365	475	504	0.16
5a	0.74	5.06	4.62	91	435	355	425	451	0.46
5b	0.45	7.78	3.94	104	312	330	421	438	0.61

[a] Inherent viscosity in chloroform at 30 °C (0.5 g/dL). [b] Weight-average molecular weight and polydispersity index (PDI) measured by GPC. [c] Glass transition temperature taken from the third DSC scan under N_2 at a heating rate of 10 °C/min. [d] Onset temperature for 5% weight loss in nitrogen, as assessed by TGA at a heating rate of 20 °C/min. [e] Absorption measured in chloroform. [f] Photoluminescence measured in chloroform with excitation at 350 nm. [g] Excitation wavelength of 350 nm for polymers **4a**,**b** and 310 nm for polymers **5a**,**b**. [h] Absolute luminescence quantum efficiency.

Table 2. Changes in PL of Thin Films of Polymers 4a,b−5a,b Quenched by DNT

△PL% (time, s) of polymer films coated on glass substrate				△PL% (time, s) of polymer films coated on optic-fiber tip			
4a	**4b**	**5a**	**5b**	**4a**	**4b**	**5a**	**5b**
23 (60)	55 (60)	41 (60)	46 (60)	31 (15)	48 (25)	26 (10)	21 (23)
45 (120)	70 (120)	60 (120)	60 (120)	38 (23)	57 (30)	74 (63)	40 (32)
64 (300)	78 (300)	81 (300)	72 (300)	44 (43)	60 (35)	87 (133)	56 (42)
75 (600)	87 (600)	96 (600)	88 (600)	46 (78)	62 (45)	91 (300)	61 (54)

was added. The mixture was purged with argon for another 10 min and then heated slowly to 90−100 °C to dissolve all the starting materials. A solution of sodium carbonate (7.0 mmol in 1.5 mL of water) was then added followed by the addition of 2−3 drops of aliqute 336. The reaction mixture was heated at the same temperature for 24 h while the light yellow solution became light green and viscous. After cooling to room temperature, the reaction mixture was poured into an excess of methanol. The resulting polymers were collected by filtration and dried in oven.

*Polymer **4a***. Starting with monomers **1a** (0.504 g, 1.0 mmol) and **2** (0.505 g, 1.0 mmol), base (0.739 g), and Pd catalyst (4.770 mg, 0.4 mol %) in 5.0 mL of solvent, polymer **4a** was obtained as yellow fibrous solids: 0.612 g. IR (film, cm^{-1}): 3020−2851 (C−H, aromatic and aliphatic), 1724 (C═O, ester), 1604 (C═C). ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 7.91 (s, 2H), 7.69 (d, 2H), 7.63 (d, 2H), 7.47 (d, 2H), 7.17 (d, 2H), 3.74 (s, 6H), 1.79−1.64 (m, 10H), 1.37 (t, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C 168.50, 147.35, 140.72, 140.09, 138.09, 133.17, 132.08, 128.79, 127.87, 127.42, 126.95, 126.34, 121.15, 77.43, 77.01, 76.59, 52.34, 31.68, 26.81, 22.71, 14.07.

*Polymer **4b***. Starting with monomers **1b** (1.061 g, 1.0 mmol) and **2** (0.505 g, 1.0 mmol), base (0.739 g), and Pd catalyst (4.770 mg, 0.4 mol %) in 5.0 mL of solvent, polymer **4b** was obtained as yellow fibrous solids: 0.850 g. IR (film, cm^{-1}): 2936−2867 (C−H, aromatic and aliphatic), 1717 (C═O, ester), 1600 (C═C). ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 7.72 (s, 2H), 7.35−7.30 (d, 4H), 7.16−7.08 (d, 4H), 5.37 (s, 2H), 4.70 (m, 2H), 3.76 (m, 2H), 2.23−0.55 (m, 99H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C 167.99, 147.32, 140.06, 139.43, 136.08, 133.81, 133.05, 131.54, 129.59, 122.82, 120.45, 117.69, 83.39, 75.04, 56.68, 56.13, 52.39, 50.00, 42.31, 39.71, 39.54, 37.71, 36.92, 36.58, 36.20, 35.81, 31.85, 31.80, 31.68, 28.25, 28.02, 27.41, 26.93, 26.80, 24.86, 24.28, 23.84, 22.84, 22.73, 22.59, 21.04, 19.33, 18.73, 14.13, 14.08, 11.88.

*Polymer **5a***. Starting with monomers **1a** (0.504 g, 1.0 mmol) and **3** (0.558 g, 1.0 mmol), base (0.739 g), and Pd catalyst (4.770 mg, 0.4 mol %) in 4.2 mL of solvent, polymer **5a** was obtained as off-white solids: 0.830 g. IR (film, cm^{-1}): 2925−2852 (C−H, aromatic and aliphatic), 1732 (C═O, ester), 1606 (C═C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 7.98 (s, 2H), 7.88−7.81 (m, 4H), 7.70 (s, 2H), 7.61−7.54 (m, 4H), 3.81 (s, 6H), 2.21−1.16 (m, 28H), 0.85 (t, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C 168.29, 151.82, 140.99, 140.28, 139.47, 133.13, 132.28, 128.88, 127.04, 126.09, 125.55, 121.50, 120.15, 77.47, 77.04, 76.62, 55.39, 52.46, 40.56, 31.82, 30.34, 30.09, 29.28, 23.91, 22.64, 14.12, 1.05.

*Polymer **5b***. Starting with monomers **1b** (1.061 g, 1.0 mmol) and **3** (0.558 g, 1.0 mmol), base (0.739 g), and Pd catalyst (4.770 mg, 0.4 mol %) in 4.2 mL of solvent, polymer **5b** was obtained as gray fibrous solids: 0.635 g. IR (film, cm^{-1}): 2930−2853 (C−H aromatic and aliphatic), 1727 (C═O, ester), 1464 (C═C). ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 7.85−7.80 (m, 4H), 7.71−7.43 (m, 4H), 5.29 (m, 2H), 4.64 (m, 2H), 2.16−0.52 (m, 121H). ^{13}C NMR ($CDCl_3$, 300 MHz): δ_C 168.01, 151.36, 140.99, 140.16, 139.24, 134.21, 131.50, 127.68, 122.83, 119.62, 77.60, 75.47, 56.67, 56.15, 55.31, 50.00, 42.28, 40.44, 39.70, 39.52, 37.74, 36.88, 36.52, 36.19, 35.80, 31.96, 31.87, 31.80, 30.49, 29.68, 29.58, 28.23, 28.02, 27.42, 24.26, 23.85, 22.82, 22.77, 22.68, 22.57, 21.02, 19.17, 18.71, 14.19, 14.13, 11.84.

Film Preparation. The polymer solution (5.0 mg in 1.0 mL of chloroform) was spin-coated onto a glass plate (microscope slide, length = 23 mm, width = 23 mm and thickness = 1 mm) at a spin rate of 1000 rpm using the Chemat Technology Spin-Coater KW-4B. The film thickness was ~65 nm, as measured using a Tencor Alpha-Step 200 surface profiler. The polymer films on optic-fiber tips were dip coated from the chloroform solution (1.5 mg/mL) and dried in air. The film thickness was measured by AFM to be ~90 nm.

Results and Discussion

Synthesis and Characterization. The general synthetic routes to the monomers and polymers are outlined in Scheme 1. The acid-catalyzed esterification of 2,5-dibromoterephthalic acid worked well with methanol to afford monomer **1a** in high yield but was not straightforward with cholesterol for the synthesis of monomer **1b**. Following a literature procedure,[21] **1b** was synthesized in 62% yield from the reaction of 2,5-dibromoterephthaloyl dichloride and cholesterol in the presence of a catalytic amount of benzyltriethylammonium chloride. ^{1}H and ^{13}C assignments of monomer **1b** were done with the aid of COSY and HETCOR experiments. Because of major overlapping in the aliphatic region, only the peaks that are vital for its identification were assigned (see Supporting Information, Table S1). The two other bisborate monomers **2** and **3** are readily available according to a known procedure[22] and from a commercial source, respectively. By cross-coupling of the two dibromide monomers **1a,b** with the two bisborate monomers **2** and **3**, a total of four homopolymers along with various copolymers can be envisioned. Thus, the Suzuki cross-coupling reaction was employed for the synthesis of homopolymers **4a,b** and **5a,b** (Scheme 1).

The obtained polymers are completely soluble in common organic solvents, such as toluene, THF, DMF, and chloroform. The inherent viscosity of these polymers in chloroform solution at 30 °C ranges from 0.25 to 0.74 dL/g (Table 1). The apparent molecular weights were measured by gel permeation chromatography (GPC) (Table 1). The viscosity values follow the order of **4a** > **4b** and **5a** > **5b**. However, the molecular weights appear to be in a reverse order (e.g., **4a** < **4b** and **5a** < **5b**), which can be attributed to a significant difference in hydrodynamic volume in GPC separation due to the different pendant groups (large cholesterol in polymers **4b** and **5b** vs small methyl group in **4a**

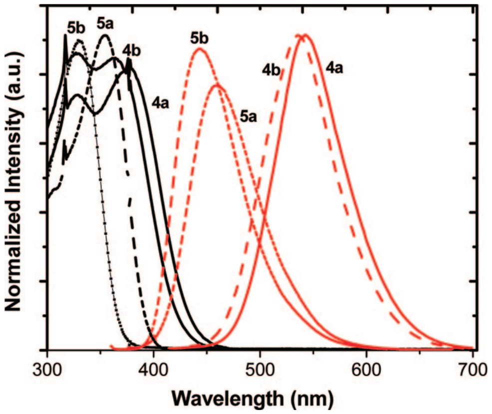


Figure 1. Absorption (black traces) and fluorescence (red traces) spectra of polymers **4a,b** (excitation at 350 nm) and **5a,b** (excitation at 310 nm) as thin films coated on glass substrate.

and **5a**). The chemical structures of the polymers are verified by NMR and IR spectroscopic methods. All the polymers exhibit a characteristic carbonyl band in the range of 1716−1734 cm^{-1}, similar to the carbonyl bands observed for monomers **1a** and **1b**. The assignment of NMR peaks for the monomers is particularly useful for verification of the polymer structures, especially for the polymers containing the cholesteryl esters. For example, the characteristic signals of the alkyl protons at 0.7−2.06 ppm from the cholesteryl moiety of monomer **1b** also appear in the ^{1}H NMR spectra of polymers **4b** and **5b** (Figure S1). Because of the high overlapping of the aliphatic protons, only important peaks in the ^{1}H and ^{13}C NMR spectra of polymers **4a,b** and **5a,b** are assigned (Table S2).

Thermal Analysis. The glass transition temperatures (T_g) and thermal stability of polymers **4a,b** and **5a,b** were characterized by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), respectively (Table 1). All the polymers appear to be amorphous with the T_g above 90 °C, as the repeated heating−cooling scans do not reveal any other transitions. The pendent cholesteryl ester is bulky and rigid enough, despite its long aliphatic chain, to impart some rigidity to polymers **4b** and **5b**, resulting in a slightly higher T_g in comparison with the methyl ester analogues **4a** and **5a**. The decomposition temperatures (T_d) of polymers are above 300 °C in nitrogen, with the exception for **4b** with a T_d of 291 °C due to its lower molecular weight ($\eta_{inh} = 0.25$ dL/g, Table 1) rather than the presence of the aliphatic cholesteryl group.

Photophysical Property. The photophysical properties of the polymers were examined in chloroform solution and as solid films. The optical data are listed in Table 1. The absorption spectra of polymers **4a** and **4b** display the two bands at around 330 nm and 365−381 nm arising from $\pi-\pi^*$ and charge-transfer (CT) transitions, respectively (Figure 1), while polymers **5a** and **5b** have only one band at 355 and 330 nm, respectively.[23,24]

Excitation of thin films of polymers **4a,b** at 350 nm and **5a,b** at 310 nm led to the emission of a yellow to green color with the maximum peaks at 438−532 nm, similar to the emission measured in solution (Table 1). Absolute luminescence quantum efficiencies of polymer films were measured by using an integral sphere. Polymers **4a,b** have a much lower quantum efficiency (7% and 16%, Table 1) than polymers **5a** (46%) and **5b** (61%). Therefore, the fluorene-based polymers **5a,b** seem to be ideal candidates for explosive detection by the fluorescence-quenching mode. To verify the emission profile of the films coated on the optic-fiber tips, the PL spectra were taken using the setup shown in Figure 4A and compared with those of the films coated on glass substrate (Figure 2). In comparison, the PL spectra obtained via the optic-fiber probe using a UV LED (375 nm) as an excitation light source are basically unchanged, since the PL spectrum of polymer **5b** was blue-shifted slightly and the bimodel PL for polymers **4a**,**b** was observed (Figure 2A). The origin of the bimodel PL is believed due to the formation of the J- and H-aggregates, although not being probed in this study. The slightly broadening in the PL spectra is deemed not to affect the sensing experiments; therefore, any changes in the fluorescence signals of these polymers upon exposure to explosive analyte can be detected via the optic-fiber probe.

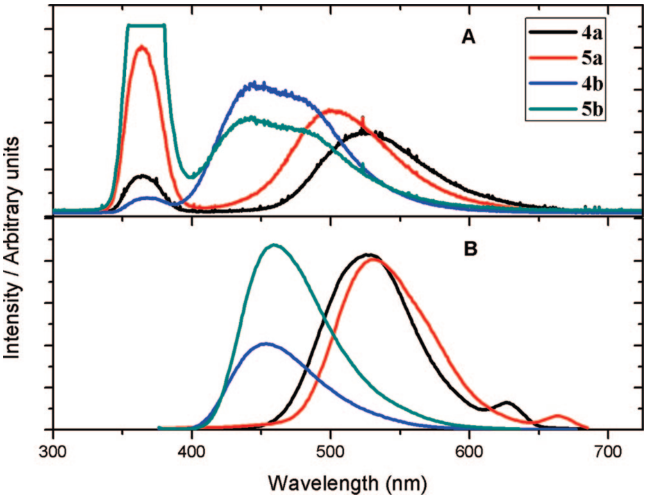


Figure 2. Emission spectra of polymers **4a,b**−**5a,b**. (A) Films (~90 nm thickness) dip coated on optic-fiber tips. The peaks at 375 nm are from the excitation light. (B) Films (~65 nm thickness) spin-coated on glass substrate.

Sensing with Polymer Films Coated on Glass Substrate. 2,4-Dinitrotoluene (DNT) was used as an explosive analyte in our study, as its equilibrium vapor pressure of 1.74 × 10^{-4} mmHg at 25 °C is relatively higher that of TNT.[25] A polymer film was exposed to the vapor of DNT powders (placed at the bottom of a 20 mL vial) at ambient temperature. The fluorescence spectra were recorded immediately after exposing the polymer film to the analyte for a specific period of time, at the excitation wavelength of 350 nm for polymers **4a**,**b** and 310 nm for polymers **5a**,**b**. The change in PL or fluorescence quenching efficiency (△PL%) is defined as $(I_0 - I)/I_0 \times 100$, where I_0 and I are the fluorescence intensity prior to and after exposure to DNT vapor, respectively. The data from an average of two readings are reported in Table 2.

A rapid PL quenching was observed for all the polymers upon exposure to DNT vapor (Figure 3A). In particular, thin film of **4b** shows a rapid quenching of its green luminescence (504 nm) by 55% in the first minute and 70% in 2 min. After 300 s, the PL spectrum virtually disappeared (Figure 3B). In comparison with polymer **4a**, polymer **4b** is twice more sensitive toward DNT vapor. Clearly, the presence of the bulky cholesteryl group (vs the methyl group) is responsible for the enhanced PL quenching, as the larger free volume or cavity facilitates trapping of the DNT molecules and thus enhances the charge transfer between the excited polymer backbone and the trapped DNT molecules. Comparison of the sensing property of polymers **5a** and **5b** reveals that the pendent ester groups have no significant effect on the PL quenching toward DNT vapor, as both polymers showed roughly 40% fluorescence quenching efficiency in 1 min and 60% in 2 min after exposure to DNT vapor. Without considering the fluorescence quantum efficiency, polymer **4b** seems more suitable for explosive sensing due to its relative high sensitivity and faster response time.

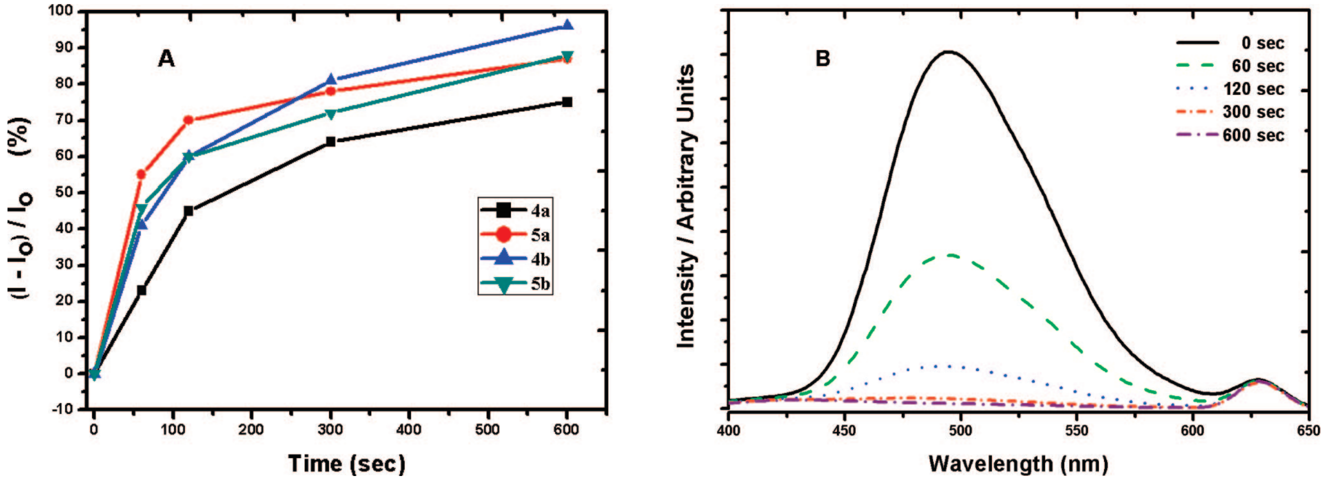


Figure 3. (A) Fluorescence quenching efficiency of thin films of polymers **4a,b**−**5a,b** on glass substrate. (B) Time-dependent PL spectra (excitation at 350 nm) of thin film of polymer **4b** upon exposure to DNT vapor at room temperature.

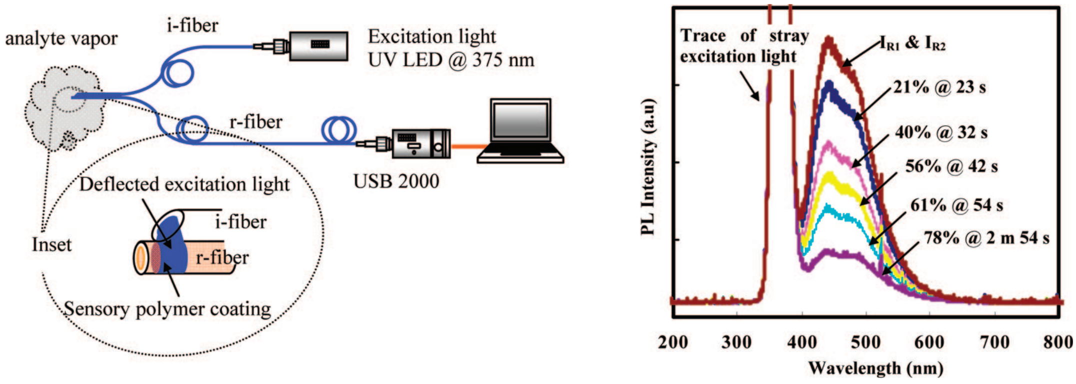


Figure 4. (A) Left: a schematic drawing of an experimental setup for fiber-optic sensing of explosives. Inset: a two-fiber probe; i-fiber is an illuminating fiber and r-fiber is a receiving fiber which is dip-coated with sensory polymer. (B) Time-dependent PL spectra (excitation at 375 nm) using polymer **5b-**coated optic-fiber probe before and after exposure to DNT vapor at room temperature.

Sensing with Polymer Films Coated on Optic-Fiber Tip. As shown in Figure 4A, the sensing probe has two fibers arranged side-by-side with one fiber (illuminating fiber, or i-fiber) serving for excitation light delivery and the other for fluorescent signal collection (receiving fiber, or r-fiber). Both are BFL37-800 large core multimode fiber with a configuration of core/cladding/jacket of 800 μm/830 μm/1400 μm. The cladding and jacket of the end segments of both fibers are stripped off. In addition, as illustrated in the inset of Figure 4A, the end face of the i-fiber is angle polished to 45° to deflect the coming excitation light toward the sidewall of r-fiber. The r-fiber is dip coated with the polymers.

In order to obtain the data from the quenching experiments with high confidence, the initial fluorescence spectrum including the recording time before exposure is taken as the first reference I_{R1}. The signal at the moment that the probe begins to be exposed to DNT vapor is also recorded as the second reference I_{R2}, which ideally should be identical or at least very close to I_{R1}. After I_{R2} is recorded, signal drops at given times are collected and compared with the reference I_{R2}. The results are summarized in Table 1.

The trend in fluorescence quenching efficiency for all the polymers using a fiber-optic probe is almost identical to that found for the films coated on glass substrate. Polymer **4b** shows the largest quenching percentage for a given time (48% at 25 s and 60% at 35 s), followed by **5b** and **5a** (Table 1). In comparison with the spectroscopic method for explosive detection using the film coated on flat glass substrate, the optic-fiber detection gives a faster response for a given quenching percentage, as shown in the case of polymer **4b** (57% at 30 s by the optic-fiber probe vs 55% at 60 s, Table 1). As mentioned before, although polymer **4b** has a higher sensitivity toward explosive analyte, its fluorescence quantum efficiency is much lower than that polymer **5b**. As shown in Figure 4B, the optic-fiber probe coated with polymer **5b** is able to give a large measurable signal (21% drop in fluorescence) at only 23 s after exposure to DNT. The fluorescence intensity continued to decrease over time when being exposed to DNT vapor and dropped by about 60% in less than 1 min. Therefore, polymer **5b** is considered a suitable candidate for optic-fiber detection of electron-deficient nitro-containing explosives. Since the data analyzer or monitor can be connected to the multiple probes via optic-fibers, the fiber-optic sensing system for explosive detection is portable, stealth, low-cost, and capable of accessing hard-to-reach areas over a long distance.

Conclusions

A series of fluorescent polymers are synthesized from the readily available monomers and tested for explosive detection as films coated on large glass substrate and small optic-fiber tips. Fiber-optic sensing of explosive analyte (DNT) has been successfully demonstrated and is found generally to be faster and more sensitive in explosive detection than using the polymer films coated on large glass substrate by a spectroscopic method. Among all the synthesized polymers, the *N*-hexyldiphenylamine-based polymers show a faster response toward DNT vapor, although they have lower fluorescence quantum efficiency. The polymer **5b** containing the fluorine moiety in the main chain and the pendant bulky cholesteryl groups has the highest fluorescence quantum efficiency and a good sensing property.

Acknowledgment. This work was supported by the Natural Science and Engineering Research Council of Canada and from the Canada Research Chairs Program. The authors thank Dr. A. I. Ianoul's group at Carleton University for doing the AFM measurement.

Supporting Information Available: ^{1}H and ^{13}C NMR assignments of monomers **1b** and polymers **4a,b** and **5a,b**; ^{1}H NMR spectra of monomer **1b** and polymer **4b**. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Fisher, M.; Cumming, C. *Proceedings of the 3rd International Aviation Security Technology Symposium*, Atlantic City, **2001**; p 288.
(2) Barshick, S. A. *J. Forensic Sci.* **1998**, *43*, 284.
(3) Yinon, J. *Trends Anal. Chem.* **2002**, *21*, 292.
(4) Hakanson, K.; Coorey, R. V.; Zubarev, R. A.; Talrose, V. L.; Hakanson, P. *J. Mass Spectrom.* **2000**, *25*, 337.
(5) Yinon, J. *Forensic and Environmental Detection of Explosives*; John Wiley & Sons: Chichester, England, 1999.
(6) Yinon, J.; Zitrin, S. *Modern Methods and Applications in Analysis of Explosives*; John Wiley & Sons: Chichester, England, 1993.
(7) Sylvia, J. M.; Janni, J. A.; Klein, J. D.; Spencer, K. M. *Anal. Chem.* **2000**, *72*, 5834.
(8) Singh, S. *J. Hazard. Mater.* **2007**, *144*, 15.
(9) McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2537.
(10) Toal, S. J.; Trogler, W. C. *J. Mater. Chem.* **2006**, *16*, 2871.
(11) Murphy, C. B.; Zhang, Y.; Troxler, T.; Ferry, V.; Martin, J. J.; Jones, W. E., Jr. *J. Phys. Chem. B* **2004**, *108*, 1537.
(12) S. W. Thomas, I.; Swager, T. M. *Adv. Mater.* **2006**, *18*, 1047.
(13) Swager, T. M. *Acc. Chem. Res.* **1998**, *31*, 201.
(14) Wang, D.; Wang, J.; Moses, D.; Bazan, G. C.; Heeger, A. J. *Langmuir* **2001**, *17*, 1262.
(15) Wang, J.; Wang, D.; Miller, E. K.; Moses, D.; Bazan, G. C.; Heeger, A. J. *Macromolecules* **2000**, *33*, 5153.
(16) Zhang, Y.; Murphy, C. B.; Jones, W. E., Jr. *Macromolecules* **2002**, *35*, 630.
(17) Zhou, Q.; Swager, T. M. *J. Am. Chem. Soc.* **1995**, *117*, 12593.
(18) Yang, J.-S.; Swager, T. M. *J. Am. Chem. Soc.* **1998**, *120*, 11864.
(19) Levitsky, I. A.; Kim, J.; Swager, T. M. *J. Am. Chem. Soc.* **1999**, *121*, 1466.
(20) Yang, J.-S.; Swager, T. M. *J. Am. Chem. Soc.* **1998**, *120*, 5321.
(21) Zhao, Z.-G.; Liu, X.-L.; Yang, Z.-X.; Tang, X.-L.; Chen, S.-H. *Youji Huaxue* **2006**, *26*, 523.
(22) Yasuda, T.; Imase, T.; Yamamoto, T. *Macromolecules* **2005**, *38*, 7378.
(23) Thomas, K. R. J.; Lin, J. T.; Tao, Y. T.; Chuen, C. H. *J. Mater. Chem.* **2002**, *12*, 3516.
(24) Thomas, K. R. J.; Lin, J. T.; Velsuamy, M.; Tao, Y.-T.; Chuen, C.-H. *Adv. Funct. Mater.* **2004**, *14*, 83.
(25) Howard, P. H.; Meylan, W. M. *Handbook of Physical Properties of Organic Chemicals*; CRC Press: Boca Raton, FL, 1997.

MA802460Q