Synthesis, Solid-Phase Reaction, Optical Properties, and Patterning of Luminescent Polyfluorenes

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ABSTRACT: The homopolymer of 9,9-di(2-(2-tetrahydropyranyloxy)ethyl)fluorene and copolymers based on 9,9-dihexylfluorene, thiophene, and 3-(2-(2-tetrahydropyranyloxy)ethyl)thiophene repeat units were obtained as patternable blue, green, and blue-green color luminescent polymers. Thermolytic and acid-catalyzed removal of the bulky tetrahydropyran (THP) group from thin solid films of the polymers was investigated. The acid-catalyzed deprotection can be carried out at a significantly lower temperature than thermolytic deprotection in the absence of acid. The effect of the acid-catalyzed deprotection of these polyfluorenes (PFs) on the photoluminescent properties was studied. Prior to deprotection, the polyfluorenes show good optical properties and high emission intensity both in solution and in the solid state. After deprotection, their optical properties were retained and their quantum yields of photoluminescence remained high, but their solubility was reduced due to the presence of hydroxyl groups. The decrease in solubility allows for their spatially controlled deposition using chemically amplified soft lithography.

Introduction

Since the first report of polymer light-emitting devices (PLEDs) based on poly(*p*-phenylenevinylene) by Burroughes et al.,[1] research on photoluminescent and electroluminescent conjugated polymers has intensified. One of the technology drivers is PLED-based full-color flat panel displays.[2] PLEDs have several advantages over small-molecule LEDs such as low cost due to solution processing and advantages over liquid crystal displays in that they are visible over a much wider range.[3]

An optimized PLED requires efficient and balanced charge injection, good and comparable mobilities for both holes and electrons, and high luminescence quantum yields.[4] Polyfluorenes (PFs) and their derivatives have drawn much attention in this area due to their good charge transport properties, high quantum yields of photoluminescence in the solid state, and exceptional electrooptical device efficiencies with long operational lifetimes. They have emerged as an attractive class of electroluminescent conjugated polymer that emit colors spanning the entire visible range with high efficiency and low operating voltage.[5] They have been much studied as active materials for potential applications such as PLEDs, organic field effect transistors (FET),[6] and organic photovoltaic cells.[7]

A critical feature in this emerging technology is device fabrication and the reproducible deposition of active material.[8] Current trends in the spatial deposition of these materials focus on three major techniques: area-selected electropolymerization,[9] photochemical patterning,[10] and nonreactive techniques. Nonreactive techniques include screen printing,[11] inkjet printing,[12] and soft lithography,[13] such as microcontact printing (μCP)[14] and micromolding in capillaries (MIMIC).[15] The technique of choice depends on the material under consideration, the substrate, and the intended application or research objective. Recently, photochemical cross-linking to produce insoluble polymer networks[16] and laser-induced thermal imaging[17] were successfully used in manufacturing devices. In the context of photolithography and soft lithography, several regioregular polythiophenes containing a 2-tetrahydropyranyl (THP) group were reported recently.[18,19] Compared with acid-catalyzed photolithography, the soft lithographic process is a low-cost technique that circumvents the use of expensive lenses and eliminates possible damage to the conjugated polymer structure due to irradiation.[19] In addition, soft lithography can pattern flexible surfaces. This strategy would appear favorable for the patterning of photoluminescent polyfluorenes (i.e., the introduction of THP groups to the side chain of the conjugated polymer, followed by deprotection) and flexible devices. In this study, the synthesis of a soluble, acid-labile, blue luminescent fluorene-based polymer, poly[9,9-di(2-(2-tetrahydropyranyloxy)ethyl)fluorene] (PTHPEF, **P1**), is reported. This polymer undergoes the solid-state, acid-catalyzed reaction shown in Scheme 1. Moreover, a series of copolymers based on the fluorene unit were synthesized in order to develop an understanding of structure−property relationships. Thiophene, 3-(2-(2-tetrahydropyranyloxy)ethyl)thiophene (THPET), or 9,9-dihexylfluorene (diHF) has been incorporated into the main chain to obtain copolymers with emissions of different color (blue, blue-green, green) and high emission intensity. The polymers retained their optical properties and quantum yields in the solid state after deprotection. Chemical amplified soft lithography has been carried out to yield polymer patterns with the same optical properties.

Experimental Section

a. Measurements. 400 MHz ^{1}H NMR spectra were obtained in CD_2Cl_2 on a Bruker AMX400 spectrometer, and 500 MHz ^{1}H and ^{13}C NMR spectra were obtained in CD_2Cl_2 on a Varian AS500 spectrometer; chemical shifts are reported in parts per million (ppm), referenced to CD_2Cl_2 (^{1}H: $\delta = 5.32$ (t); ^{13}C: $\delta = 54.00$ (quintet)). Molecular weights were measured by gel permeation chromatography (GPC) (Waters model 1515 isocratic pump) equipped with μ-Styragel columns against polystyrene standards. Polymers were eluted with THF using a flow rate of 1.0 mL/min and detected with a UV−vis detector

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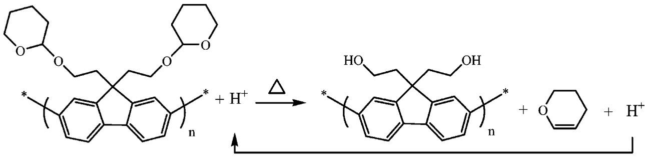
Scheme 1. Acid-Catalyzed Elimination of Dihydropyran from PTHPEF



PTHPEF

(Waters model 2487) at 254 nm. Elemental analyses were using a Carlo Erba model 1106 CHN analyzer. Low-resolution mass spectra were measured with a Hewlett-Packard 5985 GC-mass spectrometer. Matrix-assisted laser desorption/ionization time-of-flight mass spectra (MALDI−TOF) were recorded on a PerSeptive Biosystems Voyager-DE mass spectrometer using 2,5-dihydroxybenzoic acid as the matrix.

Thermogravimetric analysis (TGA) was performed at 10 °C/min on 3−5 mg of polymer sample under ambient atmosphere using a Shimadzu TGA-50 thermogravimetric analyzer. The onset temperature was estimated from the point of intersection of two lines: one extrapolated from the slope of the curve just prior to loss of the THP group and the second from the steepest part of the curve. Infrared spectra were recorded using a Bomem Michelson FTIR (120 series). Polymer samples were spin-cast on sodium chloride disks from chloroform or from chloroform/THF (80:20) solution when 5 mol % camphorsulfonic acid (CSA) was added. Thin films were heated to ~185 °C for 3 min and cooled to ambient temperature.

UV−vis absorption spectra were recorded on a Cary 3E (Varian) spectrophotometer. Photoluminescence (PL) spectra were recorded with a Photon Technology International QuantumMaster model QM-1 equipped with an extra sample compartment containing an integrating sphere. Both solution and solid-state absolute quantum yields (±10%) were obtained using an integrating sphere as previously reported.[20] Solutions were deoxygenated with high prepurified nitrogen prior to fluorescence measurements, and the sample compartment was flushed with nitrogen for thin film measurements. Fluorescent spectra of thin films, spin-cast from $CHCl_3$ on quartz, possessed an optical density of ~0.5. Spectra were recorded 22.5° normal to the incident light.

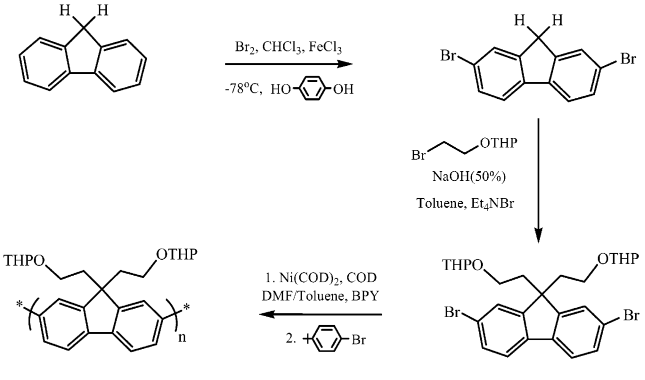
In the presence of 5 mol % camphorsulfonic acid, polymer films were spin-cast from chloroform/THF (80:20) solution. Others were spin-cast from chloroform solution. Acid-catalyzed deprotection was carried out by heating the films in the presence of 5 mol % acid at ~185 °C for 3 min. Films not containing acid were also annealed at ~185 °C for 3 min for comparison. The photographs of the PDMS stamp and the patterned polyfluorenes were taken using Nikon D1 camera.

b. PDMS Stamp. An elastomeric stamp of PDMS was molded from a photoresist-patterned template. The template was prepared by spin-casting a positive photoresist on a 4 in. diameter wafer and patterning by photolithography. The stamp was molded by pouring a prepolymer of PDMS (Sylgard 184) onto the template and curing at 60 °C overnight.

c. Materials. Fluorene, 2-(2-bromoethoxy)tetrahydro-2*H*-pyran, bis(1,5-cyclooctadiene)nickel(0) (Ni(COD)$_2$), 2,2-bipyridyl (BPY), 1,5-cyclooctadiene (COD), 9,9-dihexylfluorene-2,7-bis(trimethyleneborate) (diHFTMB), 2,5-thiophenediboronic acid, and tetrakis(triphenylphosphine)palladium (Pd(PPh$_3$)$_4$) were purchased from Aldrich and used as received. THF and toluene were dried over Na/benzophenone and freshly distilled prior to use. DMF was dried over BaO and freshly distilled prior to use.

(i) Synthesis of Poly[9,9-di(2-(2-tetrahydropyranyloxy)ethyl)fluorene] (PTHPEF, P1). PTHPEF was synthesized by the following procedure (Scheme 2). Fluorene was brominated using Br$_2$ and coupled with 2-(2′-bromoethoxy)tetrahydro-2*H*-pyran to afford 2,7-dibromo-9,9-di(2-(2′-tetrahydropyranyloxy)ethyl)fluorene (diBrTHPEF).[21] The polymer PTHPEF was prepared by the Yamamoto method.[22]

Scheme 2. Synthesis of Homopolymer PTHPEF



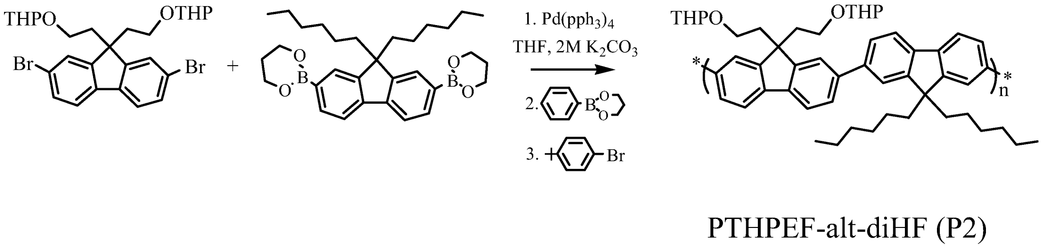
PTHPEF (P1)

2,7-Dibromofluorene (diBrF). Fluorene (10.0 g, 60.2 mmol), FeCl$_3$ (170 mg), and hydroquinone (300 mg) were dissolved in 150 mL of chloroform under nitrogen. In the absence of light, the solution was placed in a dry ice/acetone cooling bath and Br$_2$ (99.5%) (23.1 g, 144 mmol) added dropwise. The reaction mixture was warmed to room temperature and stirred overnight. The reaction mixture was quenched with 200 mL of water, washed with 10% NaHSO$_3$, and extracted with chloroform. Combined organic phases were washed with water, dried over magnesium sulfate, and concentrated under vacuum. Recrystallization of the crude product from a mixture of ethyl acetate and hexane gave 18.0 g (92.3%) of desired product. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ 7.69−7.47 (m, 6H, aromatic region), 3.88 (s, 2H).

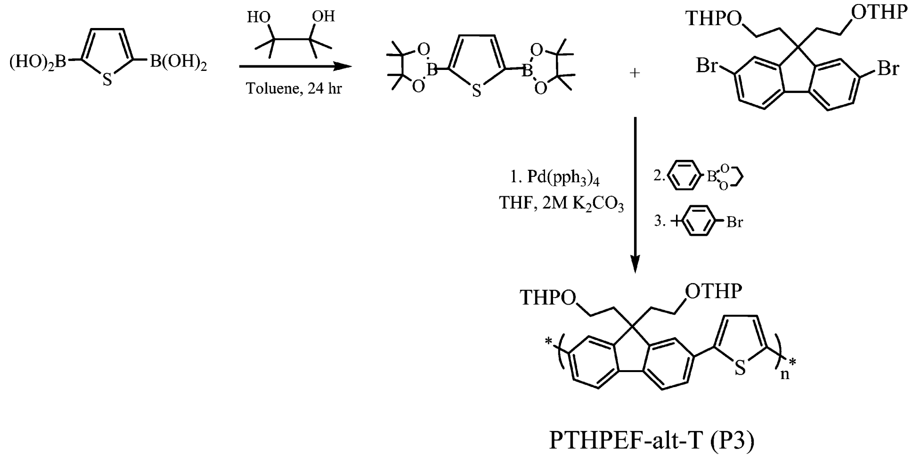
2,7-Dibromo-9,9-di(2-(2-tetrahydropyranyloxy)ethyl)fluorene (diBrTHPEF). To a solution of 5.00 g (15.4 mmol) of 2,7-dibromofluorene, 8.07 g (37.0 mmol) of 2-(2-bromoethoxy)tetrahydro-2*H*-pyran, 15 mL of toluene, and 486 mg of tetraethylammonium bromide as a phase-transfer catalyst was added 7.5 mL of a 50 wt % NaOH aqueous solution. The reaction mixture was refluxed at 90 °C for 48 h, after which it was cooled to ambient temperature. The resulting mixture was extracted with 100 mL of ethyl acetate, washed with water, dried over anhydrous magnesium sulfate, and concentrated under vacuum. The crude oily product was chromatographed on silica gel with a mixture of ethyl acetate and *n*-hexane (1/9) and recrystallized in ethanol several times to give 5.50 g (61.5% yield) of the product as a colorless crystalline: ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ 7.46−7.60 (m, 6H, aromatic region), 4.07 (t, 2H), 2.67−3.45 (m, 8H), 2.35 (t, 4H), 1.18−1.59 (m, 12H). ^{13}C NMR (500 MHz, CD$_2$Cl$_2$): δ 151.9, 139.3, 131.0, 127.5, 122.0, 121.8 (12C, aromatic region), 53.0 (1C, 9,9-C), 99.1, 62.2, 31.0, 25.9, 19.8 (10C, THP), 40.3 (2C, α-methylene), 63.6 (2C, β-methylene). MS (MALDI−TOF) *m/z* 601 (M + sodium); 603 (M + 2 + sodium); 605 (M + 4 + sodium). Anal. Calcd for $C_{27}H_{32}Br_2O_4$: C, 55.88; H, 5.56; Found: C, 55.71; H, 5.65.

PTHPEF (P1). To a vial were placed bis(1,5-cyclooctadiene)nickel(0) (Ni(COD)$_2$) (660 mg, 2.4 mmol), 2,2-bipyridyl (BPY) (375 mg, 2.4 mmol), 1,5-cyclooctadiene (COD) (0.29 mL, 2.4 mmol), and anhydrous DMF (2.5 mL) in a drybox with nitrogen. This mixture was stirred at 80 °C for 30 min to form active catalyst. The monomer 2,7-dibromo-9,9-di(2-(2-tetrahydropyranyloxy)ethyl)fluorene (diBrTHPEF) (870 mg, 1.5 mmol) in 9 mL of anhydrous toluene was added to the mixture. The polymerization proceeded at 60 °C for 6 days, and then 1-bromo-4-*tert*-butylbenzene (0.19 mL, 0.1 mmol), as an end-capping agent, was added and the mixture reacted for 24 h. The resulting polymer was purified by aluminum oxide chromatography, precipitated in methanol, and dried under vacuum for 24 h. The yield was 387 mg (61.4%). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ 7.49−7.87 (m, 6H, aromatic region), 4.15 (s, 2H), 2.45−3.49 (m, 12H), 1.26−1.61 (m, 12H). ^{13}C NMR (500 MHz, CD$_2$Cl$_2$): δ 150.9, 141.2, 140.2, 127.2, 122.5, 120.7 (12C, aromatic region); 52.6 (1C, 9,9-C), 99.2, 62.3, 31.1, 26.0, 19.9 (10C, THP), 40.7 (2C, α-methylene), 64.0 (2C, β-methylene). Anal. Calcd for $C_{27}H_{32}O_4$: C, 77.11; H, 7.67; Found: C, 71.07; H, 7.74.

Scheme 3. Synthesis of Copolymer PTHPEF-*alt*-diHF



Scheme 4. Synthesis of Copolymer PTHPEF-*alt*-T



(ii) Synthesis of Poly[9,9-di(2-(2-tetrahydropyranyloxy)ethyl)fluorene-*alt*-9,9-dihexylfluorene] (PTHPEF-*alt*-diHF, P2). 2,7-Dibromo-9,9-di(2-(2-tetrahydropyranyloxy)ethyl)fluorene (diBrTHPEF) and 9,9-dihexylfluorene-2,7-bis(trimethyleneborate) (diHFTMB) were copolymerized by Suzuki coupling[23] to yield an alternating copolymer PTHPEF-*alt*-diHF (Scheme 3).

PTHPEF-*alt*-diHF (P2). To a 20 mL Schlenk flask under nitrogen were placed 9,9-dihexylfluorene-2,7-bis(trimethyleneborate) (diHFTMB) (446 mg, 0.862 mmol), 2,7-dibromo-9,9-di(2-(2-tetrahydropyranyloxy)ethyl)fluorene (diBrTHPEF) (500 mg, 0.862 mmol), and THF (5 mL). After the solid dissolved completely, 2 M K_2CO_3 solution (1.1 mL, 2.16 mmol) and Pd(PPh_3)$_4$ (39.8 mg, 0.0345 mmol) were added, and the flask was sealed with a rubber stopper. The mixture was then heated to 60 °C for 6 days. (Tetramethyleneborate)benzene as an end-capping agent (10 mg, 0.05 mmol) was added to react continually for 24 h, and then 1-bromo-4-*tert*-butylbenzene as another end-capping agent (0.19 mL, 0.1 mmol) was added to react continually for another 24 h. THF was removed first, and then the reaction mixture was dissolved in chloroform and washed with water three times. The organic layer was dried over $MgSO_4$, and the resulting polymer was purified by aluminum oxide chromatography, precipitated in methanol, and dried under vacuum for 24 h. The yield was 582 mg (89.7%). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.50−7.89 (m, 12H, aromatic region); 4.18 (s, 2H), 2.88−3.53 (m, 8H), 2.60 (br, 4H) (THPEF); 2.17 (br, 4H), 0.77−0.82 (t, 10H) (diHF); 1.14−1.47 (m, 24H, THPEF and diHF). ^{13}C NMR (500 MHz, CD_2Cl_2): δ 150.8, 141.3, 140.2, 127.1, 122.5, 120.7 (12C, aromatic region), 52.6 (1C, 9,9-C), 40.7 (2C, α-methylene), 64.1 (2C, β-methylene), 99.2, 62.3, 31.1, 26.0, 20.0 (10C, THP) (THPEF); 152.3, 140.9, 140.7, 126.7, 122.0, 120.5 (12C, aromatic region), 56.0 (1C, 9,9-C), 41.1, 32.1, 30.3, 24.5, 23.2, 14.4 (12C) (diHF). Anal. Calcd for $C_{52}H_{64}O_4$: C, 82.94; H, 8.57. Found: C, 79.12; H, 8.48.

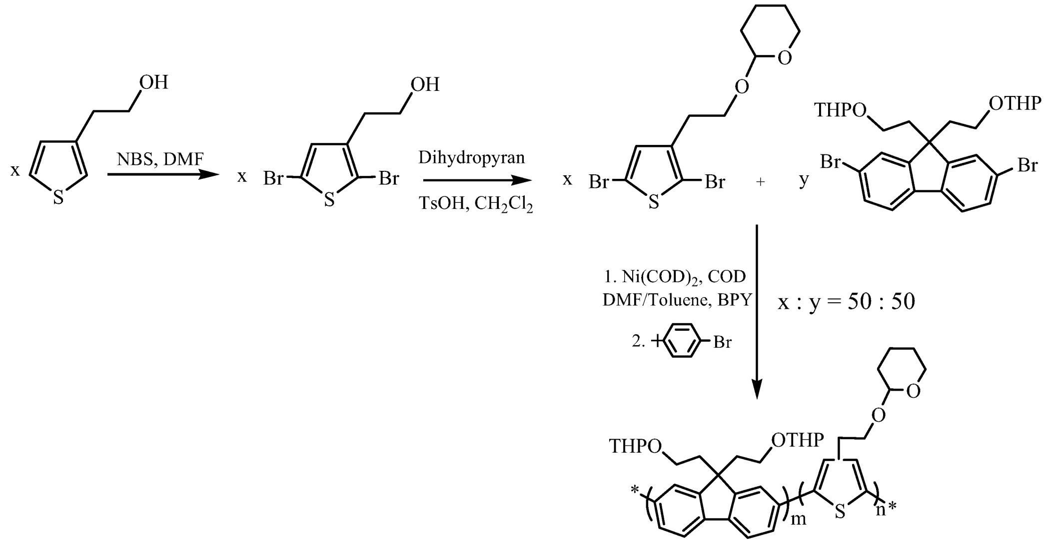
(iii) Synthesis of Poly[9,9-di(2-(2-tetrahydropyranyloxy)ethyl)fluorene-*alt*-thiophene] (PTHPEF-*alt*-T, P3). Using the same method as described above, 2,7-dibromo-9,9-di(2-(2-tetrahydropyranyloxy)ethyl)fluorene (diBrTHPEF) and 2,5-bis(tetramethyleneborate)thiophene (TMBT) were copolymerized by Suzuki coupling to yield an alternating copolymer PTHPEF-*alt*-T (Scheme 4).

2,5-Bis(tetramethyleneborate)thiophene (TMBT). To a 100 mL two-neck round-bottom flask equipped with Dean−Stark trap, molecular sieve, and refluxing condenser under nitrogen were placed 2,5-thiophenediboronic acid (0.859 g, 5 mmol), pinacol (1.30 g, 5 mmol), and toluene (40 mL). The mixture was heated under reflux for 24 h. The organic layer was separated, washed with water 3−5 times, and dried with anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the product was purified by recrystallization from ether three times to yield a white crystalline product (0.35 g, 20.8% yield). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.61 (s, 2H); 1.35−1.26 (t, 24H, CH_3).

PTHPEF-*alt*-T (P3). To a 20 mL Schlenk flask under nitrogen were placed 2,5-bis(tetramethyleneborate)thiophene (TMBT) (290 mg, 0.862 mmol), 2,7-dibromo-9,9-di(2-(2-tetrahydropyranyloxy)ethyl)fluorene (diBrTHPEF) (500 mg, 0.862 mmol), and THF (5 mL). After the solid dissolved completely, 2 M K_2CO_3 solution (1.08 mL, 2.16 mmol) and Pd(PPh_3)$_4$ (39.8 mg, 0.0345 mmol) were added, and the flask was sealed with a rubber stopper. The mixture was then heated to 60 °C for 6 days. (Tetramethyleneborate)benzene as one end-capping agent (10 mg, 0.05 mmol) was added and allowed to react for 24 h, and then 1-bromo-4-*tert*-butylbenzene as another end-capping agent (0.19 mL, 0.1 mmol) reacted for 24 h. THF was first removed, and the reaction mixture was dissolved in chloroform and washed with water three times. The organic layer was dried over $MgSO_4$, and the resulting polymer was purified by aluminum oxide chromatography, precipitated in methanol, and dried under vacuum for 24 h. The yield was 240 mg (55.4%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.12−7.77 (m, 8H, aromatic region), 4.12 (t, 2H), 2.74−3.48 (m, 8H), 2.49 (br, 4H), 1.23−1.56 (m, 12H). Anal. Calcd for $C_{31}H_{34}O_4S$: C, 74.07; H, 6.82. Found: C, 67.72; H, 6.55.

(iv) Synthesis of Poly[9,9-di(2-(2-tetrahydropyranyloxy)ethyl)fluorene-*co*-(2-(2-tetrahydropyranyloxy)ethyl)thiophene] (PTHPEF-*co*-THPET, P4). PTHPEF-*co*-THPET (50:50) was synthesized by the following procedure (Scheme 5). 3-(2-Hydroxyethyl)thiophene was brominated by NBS in DMF and protected by reacting with dihydropyran to afford 2,5-dibromo-3-(2-(2-tetrahydropyranyl-2-oxy)ethyl)thiophene (diBrTHPET).[5] Using the same coupling method as described for PTHPEF, 2,7-dibromo-9,9-di(2-(2-tetrahydropy-

Scheme 5. Synthesis of Copolymer PTHPEF-*co*-THPET



PTHPEF-co-THPET (50:50) (P4)

ranyloxy)ethyl)fluorene (diBrTHPEF) and 2,5-dibromo-3-(2-(2-tetrahydropyranyl-2-oxy)ethyl)thiophene (diBrTHPET) were copolymerized using a 50:50 feed ratio by the Yamamoto method to yield a statistically random copolymer PTHPEF-*co*-THPET.

2,5-Dibromo-3-(2-hydroxy)ethylthiophene (diBrHET). In the absence of light, a solution of NBS (7.12 g, 40 mmol) in DMF (20 mL) was added dropwise to a solution of 3-(2-hydroxyethyl)thiophene (2.56 g, 20 mmol) in DMF (20 mL). After stirring for 3 h, the reaction mixture was quenched with ice−water and extracted with ether. Combined organic phases were washed with water, dried over magnesium sulfate, and concentrated under vacuum. Distillation of the crude product gave 4.46 g (78%) of desired product. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 6.91 (s, 1H), 3.78 (t, 2H), 2.78 (t, 2H), 1.80 (s, 1H). ^{13}C NMR (500 MHz, CD_2Cl_2): δ 140.2, 132.0, 111.1, 109.8 (4C, thienyl ring), 33.3 (1C, α-methylene), 62.1 (1C, β-methylene). MS *m/z* (based on ^{79}Br): 284 M$^+$; 286 $(M + 2)^+$; 288 $(M + 4)^+$. Anal. Calcd for $C_6H_6Br_2OS$: C, 25.20; H, 2.11. Found: C, 25.09; H, 2.16.

2,5-Dibromo-3-(2-(2-tetrahydropyranyl-2-oxy)ethyl)-thiophene (diBrTHPET). To a solution of 2,5-dibromo-3-(2-hydroxy)ethylthiophene (4.29 g, 15 mmol) and freshly distilled dihydropyran (2.52 g, 30 mmol) in 80 mL of dry chloroform, cooled to 0 °C, was added 29 mg (0.15 mmol) of *p*-toluenesulfonic acid monohydrate under N_2. After stirring for 10 min at 0 °C, for 2 h at room temperature, the mixture was poured into ice−water and extracted with chloroform. The organic phase was combined, washed with saturated sodium hydrogen carbonate solution and water, and dried over magnesium sulfate. The crude product, obtained by removal of solvent, was chromatographed on silica gel (Silica Gel 60, EM Science) with chloroform to afford 4.16 g (75%) of the desired monomer. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.25 (s, 1H), 4.60 (s, 1H), 3.91−3.48 (m, 4H,), 2.84 (t, 2H), 1.82−1.49 (m, 6H). ^{13}C NMR (500 MHz, CD_2Cl_2): δ 140.7, 132.3, 110.7, 109.5 (4C, thienyl ring), 99.1, 62.5, 31.2, 26.1, 20.0 (5C, THP), 30.6 (1C, α-methylene), 66.4 (1C, β-methylene). MS *m/z* (based on ^{79}Br): 368 M$^+$; 370 $(M + 2)^+$; 372 $(M + 4)^+$. Anal. Calcd for $C_{11}H_{14}Br_2O_2S$: C, 35.70; H, 3.81. Found: C, 35.72; H, 3.76.

PTHPEF-*co*-THPET (50:50) (P4). To a vial were placed bis(1,5-cyclooctadiene)nickel(0) ($Ni(COD)_2$) (440 mg, 1.6 mmol), 2,2-bipyridyl (BPY) (250 mg, 1.6 mmol), 1,5-cyclooctadiene (COD) (0.20 mL, 1.6 mmol), and anhydrous DMF (1.5 mL) in a drybox with nitrogen. This mixture was stirred at 80 °C for 30 min to form active catalyst. The monomers 2,7-dibromo-9,9-di(2-(2-tetrahydropyranyloxy)ethyl)fluorene (diBrTHPEF) (290 mg, 0.5 mmol) and 2,5-dibromo-3-(2-(2-tetrahydropyranyl-2-oxy)ethyl)thiophene (diBrTHPET) (185 mg, 0.5 mmol) in 6 mL of anhydrous toluene were added to the mixture. The polymerization proceeded at 60 °C for 6 days, and then 1-bromo-4-*tert*-butylbenzene as end-capping agent (0.19 mL, 0.1 mmol) was added and reacted for another 24 h. The resulting polymer was purified by aluminum oxide chromatography, precipitated in methanol, and finally dried under vacuum for 24 h. The yield was 202 mg (64.1%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.32−7.79 (m, 7H, aromatic region), 4.14 (s, 3H), 2.43−3.47 (m, 18H), 1.24−1.64 (m, 18H). Anal. Calcd for $C_{38}H_{46}O_6S$: C, 72.38; H, 7.30. Found: C, 67.10; H, 7.33.

Results and Discussion

1. Polymer Structure. The structure of these polymers was confirmed by NMR spectroscopy. Homopolymer **P1** gave ^{1}H NMR resonance peaks at 7.49−7.87 and 4.15 ppm assigned to the aromatic protons of the fluorene ring and the methine of the THP group, respectively. ^{13}C NMR of this homopolymer exhibited 14 resonance peaks. The six peaks at 150.9, 141.2, 140.2, 127.2, 122.5, and 120.7 ppm were assigned to fluorene ring carbons.[22b] The observed peaks at 99.2, 62.3, 31.1, 26.0, and 19.9 ppm are characteristic of the THP group.[24] Peaks at 40.7 and 64.0 ppm were assigned to α- and β-methylene carbons, respectively. The peak at 52.6 ppm was assigned to the 9,9-carbon.

Alternating copolymer **P2** gave resonance peaks at 7.50−7.89 ppm assigned to the aromatic protons of the fluorene ring, one resonance peak at 4.18 ppm assigned to the methine of THP group, and two α-methylene resonance peaks at 2.60 and 2.17 ppm corresponding to THPEF and diHF units, respectively. Resonance peaks were observed in the ^{13}C NMR spectra of the copolymer **P2** at 99.2, 64.1, 62.3, 40.7, 31.1, 26.0, and 20.0 ppm, assigned to the seven carbons on the THPEF unit, and at 41.1, 32.1, 30.3, 24.5, 23.2, and 14.4 ppm, attributed to the six carbons on the hexyl chain. In the aromatic region, peaks were observed at 150.8, 141.3, 140.2, 127.1, 122.5, and 120.7 ppm, assigned to the fluorene ring carbons of THPEF, and at 152.3, 140.9, 140.7, 126.7, 122.0, and 120.5 ppm, assigned to the fluorene ring carbons of diHF. The two peaks of 9,9-carbons at 52.6 and 56.0 ppm were attributed to THPEF and diHF, respectively.

Table 1. Molecular Weight of Polyfluorenes

polymers	M_n	M_w	PDI
P1	23 800	34 300	1.44
P2	23 800	48 200	2.02
P3	3 700	3 800	1.03
P4	10 800	26 000	2.42

Table 2. Thermal Properties of Polyfluorenes

		in the absence of acid		in the presence of 5 mol % camphorsulfonic acid	
polymers	theor wt loss[a] (%)	onset (°C)	obsd wt loss (%)	onset (°C)	obsd wt loss (%)
P1	40	240	40	120	40
P2	22	360	20	150	22
P3	34	200	34	110	34
P4	40	230	38	140	40

[a] Based on THP groups removal.

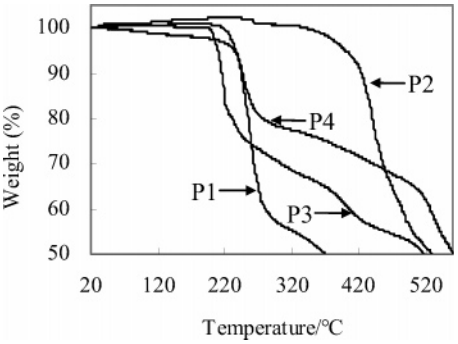


Figure 1. TGA thermograms of polyfluorenes in the absence of acid: **P1** (PTHPEF), **P2** (PTHPEF-*alt*-diHF), **P3** (PTHPEF-*alt*-T), and **P4** (PTHPEF-*co*-THPET).

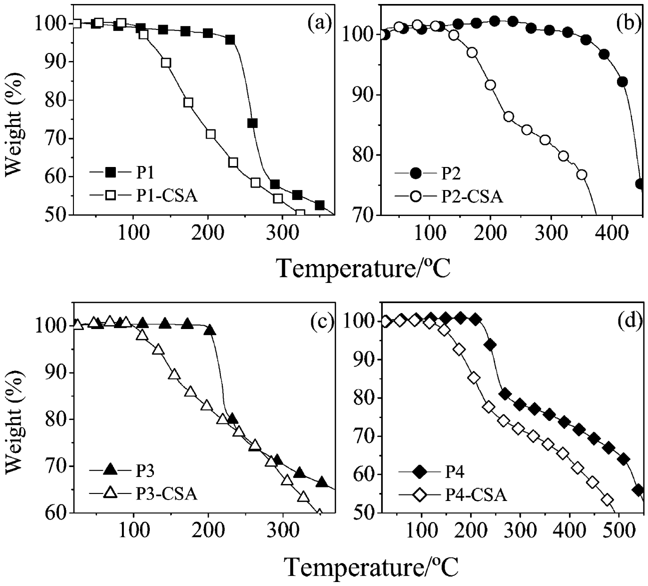


Figure 2. TGA thermograms of polyfluorenes in the absence and presence of 5 mol % camphorsulfonic acid: (a) **P1** (PTHPEF), (b) **P2** (PTHPEF-*alt*-diHF), (c) **P3** (PTHPEF-*alt*-T), and (d) **P4** (PTHPEF-*co*-THPET).

Alternating copolymer **P3** gave resonance peaks at 7.12−7.77 ppm assigned to aromatic protons of the fluorene and thienyl ring, and one resonance peak at 4.12 ppm assigned to the methine of THP group, and one α-methylene resonance peak at 2.49 ppm corresponding to the THP group. Random copolymer **P4** (THPEF:THPET/50:50) gave resonance peaks at 7.32−7.79 ppm assigned to aromatic protons of the fluorene and thienyl ring and one resonance peak at 4.14 ppm assigned to the methine of THP group. The composition of **P4** was determined from the ratio (7.0:3.0) of integrals of the peaks of aromatic protons ($6m\% + 1n\%$) and methine ($2m\% + 1n\%$) to yield m:n = 50:50, which is consistent with the feed ratio.

The molecular weight and polydispersity index of these four polyfluorenes are shown in Table 1. The molecular weights and the polydispersities of **P1**, **P2**, and **P4** are typical of fluorene-based polymers prepared by Yamamoto or Suzuki coupling. However, **P3** possessed a lower molecular weight. This might result from its solubility, which was noticeably worse because of the absence of a side chain on the thienyl ring. Another reason may be the lower reaction temperature employed. Usually the molecular weights can be increased with temperature, but in this case the temperature was limited to 65 °C to prevent cleavage of the THP.

2. Thermal Properties and Solid-State Reaction. THP is a relatively thermally stable protecting group. For example, poly(3-(2-(2-tetrahydropyranyloxy)ethyl)-thiophene) (PTHPET) was reported stable up to 220−230 °C.[18a,b] For **P1** and **P4**, a significant loss in mass is observed by TGA above this temperature, as shown in Table 2. **P3** exhibits a lower deprotection temperature, which is ascribed to its lower molecular weight.[19a] In contrast, **P2** shows quite a high deprotection temperature, owing to its higher molecular weight and the better stabilizing effect of the alkyl side chains on the main chain. The incorporation of 9,9-dihexylfluorene (diHF) groups into the chain might actually increase the rigidity of the polymer and increase molecular interactions by promoting side chain aggregation. The THP functionality represents 40 wt % of **P1** and **P4**, 22 wt % of **P2**, and 34 wt % of **P3**. The observed weight losses of **P1**, **P2**, **P3**, and **P4** are 40, 20, 34, and 38 wt %, which are consistent with calculated losses of mass due to thermolytic cleavage of the THP group and elimination of dihydropyran.

Using the same scan rate of 10 °C/min, the onset temperatures required to remove the THP group from the polyfluorenes (110−150 °C) are much lower in the presence of 5 mol % camphorsulfonic acid (mol % based on the THP unit), as shown in Figure 2. The observed weight losses of **P1**, **P2**, **P3**, and **P4** are 40, 22, 34, and 39 wt %, consistent with the theoretical weight losses. Only 5 mol % acid is needed to get full deprotection of the THP group, indicating the removal of THP is catalyzed similar to that reported for polythiophenes.[18] FTIR analysis shows the emergence of a broad signal at ~3450 cm^{-1} upon acid-catalyzed reaction at 185 °C due to the formation of the hydroxyl group (Figure 3). FTIR signals assigned to the THP group, originally at 1030−1130 and 2940 cm^{-1}, diminish upon acid-catalyzed reaction. The appearance of one peak at 1742 cm^{-1} is due to the camphorsulfonic acid. The camphorsulfonic acid has another strong peak at ~2940 cm^{-1}, which interferes with the peak due to the polymer at 2940 cm^{-1}. Furthermore, no obvious new fluorenone peaks were observed at 1717, 1606, and 1457 cm^{-1},[25] although the acid-catalyzed reaction was carried out in the presence of air. This statement is confirmed by PL spectra of deprotected polyfluorenes, which shows the absence of the characteristic green emission peak. Therefore, the solid-state reaction can be carried out at rather lower temperatures to avoid significant oxidation

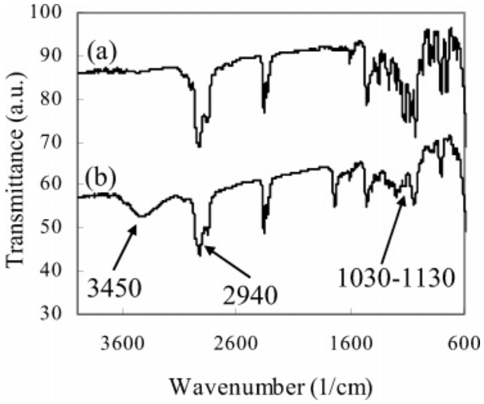


Figure 3. FTIR of **P3** (PTHPEF-*alt*-T) before (a) and after (b) acid-catalyzed deprotection.

in ambient environment and loss of fine optical properties.

3. Optical Properties. The optical properties of the polyfluorenes in THF solution and in the solid state before/after deprotection and after annealing are summarized in Table 3.

a. UV−Vis Absorption and PL Properties of Polyfluorenes Prior to Deprotection. The UV−vis and PL spectra of polyfluorenes in THF solution and in the solid state are shown in Figure 4. Photographs of polyfluorenes in solvent ($CHCl_3$) and in the form of films under visible and UV light are shown in Figure 5.

The maximum absorption wavelengths of **P1**, **P2**, **P3**, and **P4** in solution are 373, 387, 402, and 379 nm and in the solid state are 375, 389, 410, and 380 nm, respectively. The absorption spectra show the same character in that λ_{max} of films is red-shifted compared to that in solution. λ_{max} of **P3** in solution and in the solid state are 29 and 35 nm higher than those of **P1**, owing to higher electron density of thienyl ring than fluorene and lower band gap of P3. λ_{max} of **P4**, possessing thienyl rings bearing a THP group, is very close to **P1**, differing by only 5−6 nm. This might be due to the random composition of **P4**. λ_{max} of **P4** is expected to be due to the fluorene block. The thienyl block contributes to the lower energy region of the absorption spectra, resulting in a slightly broader full width at half-maximum (fwhm) (86 nm for **P4** vs 72 nm for **P1** in solution). The THP side chains on the thienyl ring of **P4** are also expected to twist the thienyl ring and cause a blue shift of absorption, compared to **P3**, which does not possess a side chain on thienyl ring. Compared to another alternating polymer, described in the literature, with different side chains on both fluorene and thienyl rings,[26] **P4** possesses a blue-shifted λ_{max}. This might also be due to the random composition[27] of **P4** and the less effective conjugation for sterically hindered THP groups. A slightly narrower fwhm (around 66 nm) for the literature polymer supports this explanation.

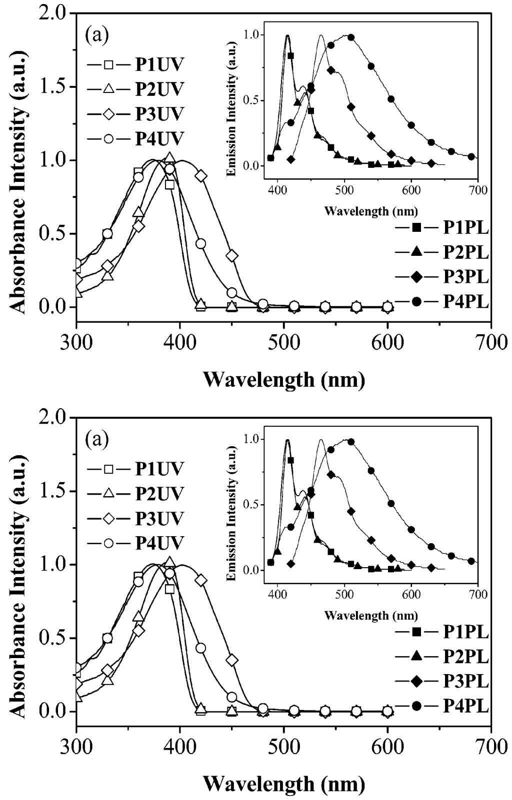


Figure 4. UV−vis and PL spectra of polyfluorenes in solution (a) and the solid state (b) **P1** (PTHPEF), **P2** (PTHPEF-*alt*-diHF), **P3** (PTHPEF-*alt*-T), and **P4** (PTHPEF-*co*-THPET).

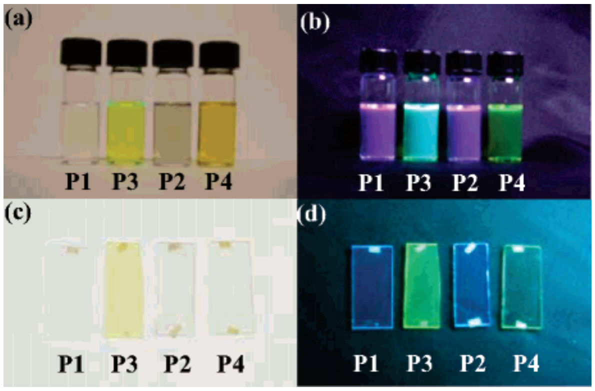


Figure 5. Polyfluorenes in solvent ($CHCl_3$) under visible (a) and UV (b) light (λ = 254 nm) and in the form of films under visible (c) and UV (d) light: **P1** (PTHPEF), **P2** (PTHPEF-*alt*-diHF), **P3** (PTHPEF-*alt*-T), and **P4** (PTHPEF-*co*-THPET).

The maximum emission wavelengths of homopolymer **P1** and alternating copolymer **P2** in solution (414 and 416 nm, respectively, violet-blue color) and in the solid state (421 and 423 nm, respectively, blue color) are quite similar, and both of their PL spectra are sharp, indicating that the effect of THP vs hexyl side chains attached to the fluorene backbone on the emission spectra is very small. Although both **P1** and **P2** possess almost quantitative absolute quantum yields in solution (Φ_{fl}: 1.00

Table 3. Optical Properties of Polyfluorenes

	solution (THF)			solid state			films-deprotected			films-annealed	
polymers	λ_{max}(abs), nm	λ_{max}(em), nm	Φ_{fl}	λ_{max}(abs), nm	λ_{max}(em), nm	Φ_{fl}	λ_{max}(abs), nm	λ_{max}(em), nm	Φ_{fl}	λ_{max}(abs), nm	λ_{max}(em), nm
P1	373	414	1.00	375	421	0.37	380	428	0.37	380	431
P2	387	416	0.96	389	423	0.27	389	427	0.22	391	427
P3	402	465	0.76	410	501	0.36	412	507	0.36	406	501
P4	379	502	0.62	380	539	0.29	381	557	0.29	381	540

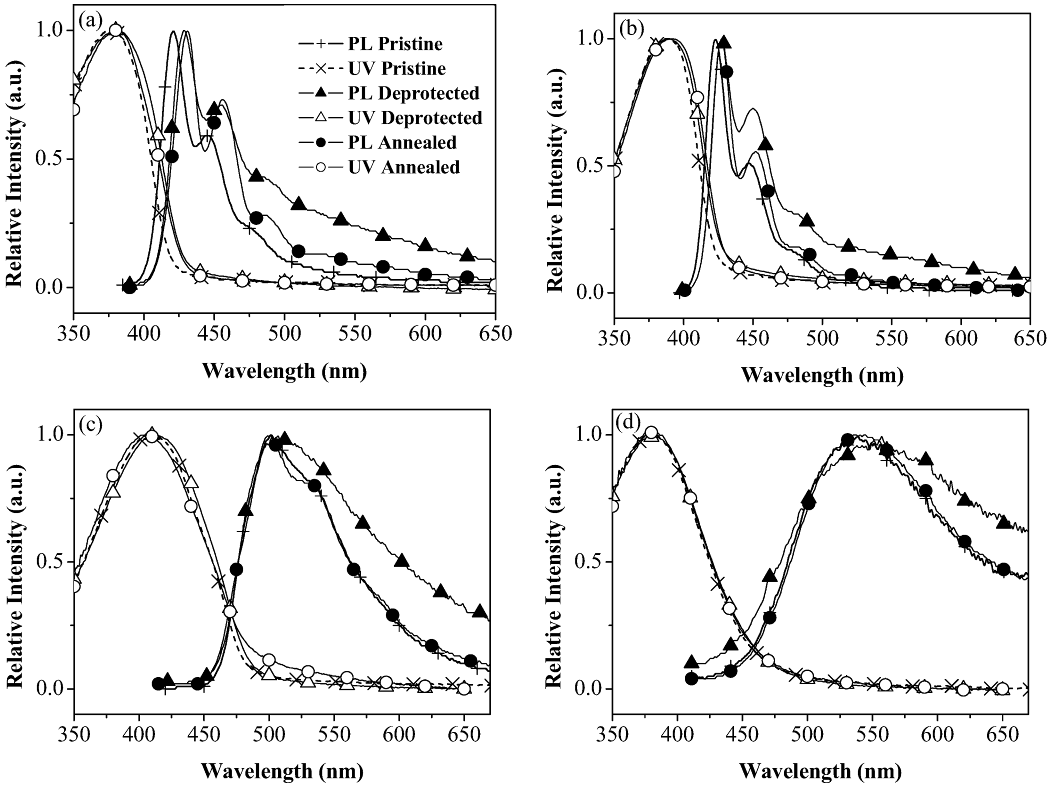


Figure 6. UV−vis and PL spectra of polyfluorenes in the solid state before/after deprotection and after annealing: (a) **P1** (PTHPEF), (b) **P2** (PTHPEF-*alt*-diHF), (c) **P3** (PTHPEF-*alt*-T), and (d) **P4** (PTHPEF-*co*-THPET).

and 0.96), their quantum yields in the solid state (Φ_{fl}: 0.37 and 0.27) are different. The higher quantum yield for **P1** may indicate that the bulky THP side chain may be more efficient at preventing molecular interaction.[28] The introduction of THP groups to the blue luminescent polyfluorenes on one hand facilitates patterning of the polymer, but it also improves the emission intensity of the polymer.

The maximum emission wavelengths of alternating copolymer **P3** in solution and in the solid state are 465 nm (blue-green color) and 501 nm (cyan). Its quantum yield in solution and in the solid state are still high (0.76 and 0.36, respectively). The quantum yield of **P3**, especially in the solid state, is surprisingly high, given that no side chain is present on the thienyl ring to prevent interchain interaction. Other similar copolymers with different side chains on the fluorene in the literature[23a,26,29] have slightly lower values in solutions and very low values in solid films. The reason may be due to the bulky THP side chains and the contribution of end-capping groups in **P3**. Otherwise, the uncapped end groups may introduce some defects to the emitting structure.[30]

The emission wavelengths of random copolymer **P4** in solution and in the solid state are 502 nm (cyan) and 539 nm (green). Moreover, its emission intensity is high both in solution and in the solid state (Φ_{fl}: 0.62 and 0.29), so that strong emission can be observed under UV light as shown in Figure 5. In addition, compared to **P3** and to other alternating copolymers with side chains on both fluorene and thienyl rings, **P4** exhibits a red-shifted emission wavelength, although its absorption wavelength is blue-shifted. The reason may be also attributed to the random structure of copolymer **P4**. The different units of fluorene and thiophene may form two kinds of block, polyfluorene block, polythiophene block, and even graded polymers. The higher energy polyfluorene block might therefore be transferring energy to lower energy polythiophene blocks to yield enhanced green emission.[29,31]

b. UV−Vis Absorption and PL Emission Properties of Polyfluorenes after Deprotection. The UV−vis and PL spectra of the polyfluorenes as a pristine film, after annealing at 185 °C, and after deprotection are shown in Figure 6. **P1** and **P2** have only fluorene repeat units, their absorption onsets after deprotection are slightly red-shifted compared with the pristine films, and their corresponding maximum emission wavelengths are also red-shifted. This phenomenon was reported in polydioctylfluorene (PFO) as a result of extended conjugation, i.e., formation of β-phase[32] upon extended annealing or upon solvent swelling stress. Absorption and emission spectra of annealed films are similar to that of the deprotected films, indicating that the small variations in spectra of the deprotected polymers are indeed due to the annealing process. **P3** and **P4** both possessed fluorene and thienyl units. Their absorption and emission spectra after annealing are similar to that of the pristine films. This may be related to the polyfluorene structures, which are different from PFO and do not form β-phase such as in the case for polyfluorene with branched side chain.[6d] In our case, the incorporation of thiophene units might prevent the formation of the β-phase. The spectra after deprotection are similar to that of the annealed films, again showing that the removal of THP groups has no obvious effect on the spectra of the polymers. However, the hydroxy groups after the removal of THP may induce a small effect on PL spectra, as seen from the broader PL emission peaks for **P3** and **P4**. This effect is not pronounced for all of deprotected polymers, as also can be inferred by the small variations in quantum efficiency. Pei et al.[33] reported a polyfluorene with hydroxy group in the side chain and found that dominating yellowish-orange emission originates from hydrogen-bonding-induced self-assembled aggregates of solutions and films spin-cast from non-hydrogen-bonding solvents but not in a solution with hydrogen-bonding solvents. Removal of THP in the present case takes place in the solid state, and a self-assembled process is difficult to develop during deprotection and thus no obvious emitting aggregates at lower energy are observed. The high emission quantum yields in the solid state were retained, demonstrating that the deprotection process did not damage the emission. Furthermore, the low processing temperature and rather short time of heating reduced the formation of fluorenone, as evidenced by the absence of green emission in the emission spectra of deprotected **P1**−**P4** films.

4. Chemically Amplified Soft Lithography. Chemically amplified soft lithography was demonstrated using a copolymer based on 3,4-ethylenedioxythiophene (EDOT) and a thiophene unit bearing a THP group.[19] An insoluble pattern of the polythiophene was fabricated via removal of the THP groups using an acid-catalyzed solid-state reaction. The catalytic amount of acid was transferred from an “inked” PDMS stamp to the surface of the polymer. The concentration of the acid affected the quality of the pattern. A similar procedure was followed for THP-protected polyfluorenes. A higher temperature for the solid-state reaction in copolyfluorenes was used. A scheme of the procedure is shown in Figure 7a. All the copolymers described in this work were patterned this way. For example, **P2** was spin-cast onto a glass substrate from a chloroform solution to yield a film with thickness $\sim$100 nm. The patterned surface of PDMS stamp was immersed in a solution of 0.01 M camphorsulfonic acid in THF and hexane (50/50) for 3 s. A photograph of the stamp pattern is shown in Figure 7b. The “inked” stamp was dried in air for 30 s and then pressed lightly on top of the polymer film for 10−15 s, thereby transferring the acid to the surface. The resulting film was thermally treated at 185 °C for 15 s under ambient atmosphere. The acid-catalyzed deprotection reaction took place in the solid state and resulted in cleavage of the THP group and elimination of dihydropyran in the regions where acid was deposited. These regions became insoluble by virtue of the residual hydroxyl group and the change in polarity. Development in chloroform provided a positive image of the stamp. Figure 7c shows emission from the patterned polymer when exposed to UV light.

P1 and **P4** possess THP groups on every repeat unit, whereas **P2** and **P3** bear THP groups on 50% of the repeat units. Nevertheless, **P2** and **P3** can be successfully patterned. The removal of the THP functional group from side chains is sufficient to deprotect the polymers and to form a patterned image, indicating that other functional groups may be attached to the side chains.

Compared with other methods, such as photolithography, the soft lithographic process eliminates possible damage to the luminescent polymer structure, such as fluorenone formation.[34] Figure 6, showing PL spectra of the **P1**−**P4** films before and after acid-catalyzed deprotection, indicates the PL spectra are unchanged. The PL spectra of patterned **P2** were measured and were found similar to the PL spectra of the deprotected film as shown in Figure 7d. Furthermore, the quantum

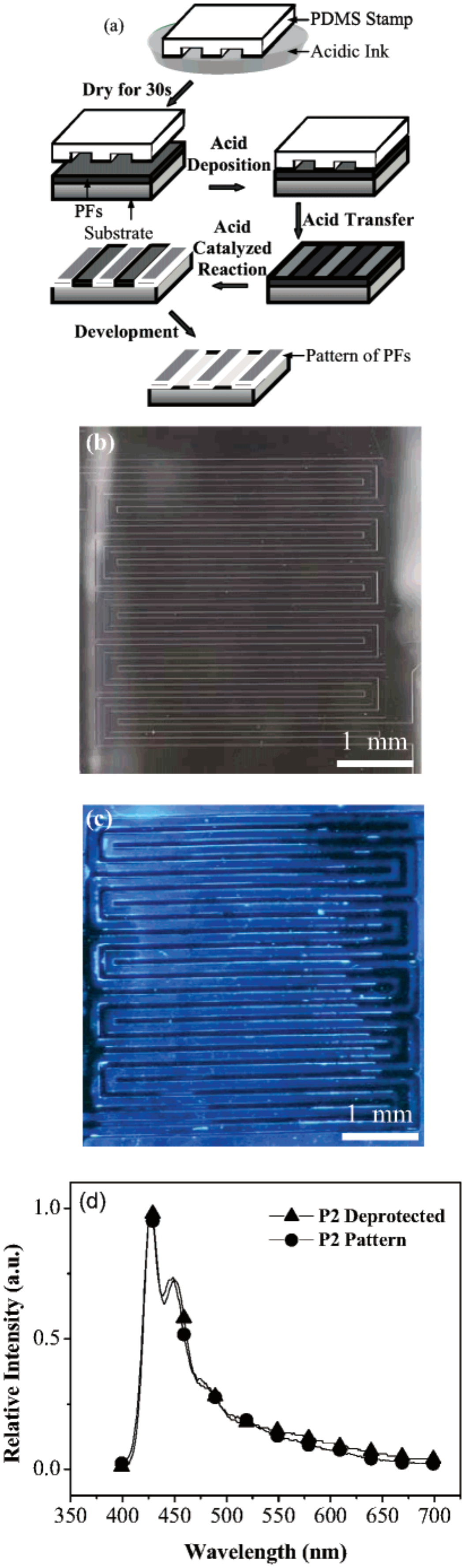


Figure 7. (a) Scheme depicting chemically amplified soft lithographic process, (b) a micrograph of PDMS stamp, (c) an emission of patterned **P2** (PTHPEF-*alt*-diHF) under UV light, and (d) PL spectra of deprotected and patterned **P2**.

yields of these polymer films exhibited no change after acid-catalyzed deprotection, indicating their potential application in patterned PLEDs.

Conclusions

Blue, green, and blue-green color fluorene-based polymers, PTHPEF, PTHPEF-*alt*-diHF, PTHPEF-*alt*-T, and PTHPEF-*co*-THPET, containing THP functional groups, have been synthesized by Yamamoto and Suzuki coupling reactions. The solid-state removal of dihydropyran from the side chain was confirmed by thermogravimetry and spectroscopic analysis. The acid-catalyzed cleavage of the THP group in the presence of acid occurred at much lower temperature than homolytic removal of the THP group in the absence of acid. The pristine polyfluorenes exhibit exceptional luminescent properties in solution and in the solid state because the bulky THP group reduces the interchain interaction of the polymers. Moreover, after deprotection, the deprotected polyfluorenes possess optical properties and quantum yields that are similar to the pristine polymers. The slight change of absorption and emission wavelength is attributed to the influence of thermal annealing. Because of the short length of side chains and H-bonding (via terminal hydroxyl groups), the removal of the THP groups causes the polymers to become insoluble. Chemically amplified soft lithography can be used to pattern the luminescent polymers. In summary, the design of conjugated polymers bearing THP groups, or other protecting groups, might be a general method for patterning luminescent polymers. These patternable polyfluorenes with bright blue, green, and blue-green color emission are promising candidates in the fabrication of multicolor emitting LED device.

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Supporting Information Available: NMR spectra of **P1**−**P4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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