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Blue-Light-Emitting Cationic Water-Soluble Polyfluorene Derivatives with Tunable Quaternization Degree

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ABSTRACT: The design, synthesis and characterization of novel blue emission cationic water-soluble conjugated polymers based on the polyfluorene (PF) derivatives with amino-terminal groups are described. Water solubility was realized through quaternization of the amino group, which permits a control of the cationic degree, which in turn determines the solubility of the polymers in organic solvents and water. Better solubility in polar solvents was accompanied by a spectral blue shift for polymers with a higher quaternization degree. In the presence of a trace amount of some weak organic acids, the neutral polymer also showed a high solubility in water. Instead of forming a quaternized salt, the ^{1}H NMR spectra indicated that only electrostatic interaction existed between the acid and the amino-terminal groups, which increased the affinity of the polymers with those polar solvents. In addition to the special solubility, good thermal stability as well as the intense fluorescence both in solutions and as films endows this series of materials with the status of most attractive candidates as the transporting/emitting layer in multilayer device fabrication.

Introduction

Conjugated polymers have been widely used as light-emitting and hole/electron transporting materials in light-emitting diodes. The solubility of conjugated polymers could be greatly improved by attaching flexible side chains or large substituents, and through the modification of the pendant groups, the physical, mechanical and processing properties of the materials could be tunable. Through attaching ionic functions such as carboxylic acid groups to the main chain, an important subset of functional polymers as the water-soluble polymers was developed.[1]

Water solubility of conjugated polymers may offer a lot of new application opportunities. Potential applications of water-soluble conjugated polymers include the construction of active layers in organic light-emitting diodes through layer-by-layer self-assembly approach,[2] as buffer layer and emissive layer materials in inkjet printing fabricated organic LEDs,[3] and as highly sensitive fluorescent sensory materials in living bodies.[4,5] The applications generally favor high molecular weights and high photoluminescence (PL) efficiencies and require different ionic types. Many water-soluble polymers have been synthesized by homo- and copolymerization as well as by polymer analogous reactions.[6]

Water solubility of semiconducting conjugated polymers was first demonstrated in 3-substituted polythiophenes[7,8] and was then extended to poly(*p*-phenylenevinylene)- (PPV-) based[9] and poly(*p*-phenylene)- (PPP-) based polymers.[10−12] Among them, water-soluble PPP derivatives have been widely investigated.[12−19] Recent publications have shown that PPP polyelectrolytes could be obtained with high molecular weights, controlled physical properties, and desired solubility.[20−24] However, most of the polyelectrolytes investigated so far are functionalized with terminal carboxylate or sulfonate groups, which are anionic polyelectrolytes. It is sometimes required that also cationic polymers be used as in the case of multilayer deposition from solution.[25−27] The search of soluble cationic conjugated polymers becomes an additional interesting target.

On the basis of our previous design of using tertiary amine as the functional group for the neutral polymers, several water-soluble polymers were synthesized through adjusting the quaternization conditions. Because of their charged nature and related water solubility, these molecules are potential candidates that could be processed at the molecular level by the extremely versatile layer-by-layer sequential adsorption technique.[2c]

Experimental Section

General Data. The NMR spectra were collected on a Bruker ACF 300 spectrometer with chloroform-*d* or methanol-*d* as solvent and tetramethylsilane as internal standard. FT-IR spectra were recorded on a Bio-Rad FTS 165 spectrometer by dispersing samples in KBr. UV−vis spectra were recorded on a Shimadzu 3101 PC spectrometer. Fluorescence measurement was carried out on a Perkin-Elmer LS 50B photoluminescence spectrometer with a xenon lamp as a light source. Thermogravimetric analyses (TGA) were conducted on a Du Pont Thermal Analyst 2100 system with a TGA 2950 thermogravimetric analyzer under a heating rate of 10 °C/min and a nitrogen flow rate of 70 mL/min. Differential scanning calorimetry (DSC) was run on a Du Pont DSC 2910 module in conjunction with the Du Pont Thermal Analyst system at a heating rate of 20 °C/min. Elemental microanalyses were carried out by the Microanalysis Lab of the National University of Singapore. GPC analysis was conducted with a Waters 2696 separation module equipped with a Waters 410 differential refractometer HPLC system and Waters Styragel HR 4E columns using polystyrene as standard and THF as eluant.

Materials. Reagents and chemicals were purchased from Aldrich Chemical Co. unless otherwise stated. Tetrahydrofuran (THF) was purified by distillation from sodium in the

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presence of benzophenone. Dimethyl sulfoxide (DMSO) was distilled prior to use.

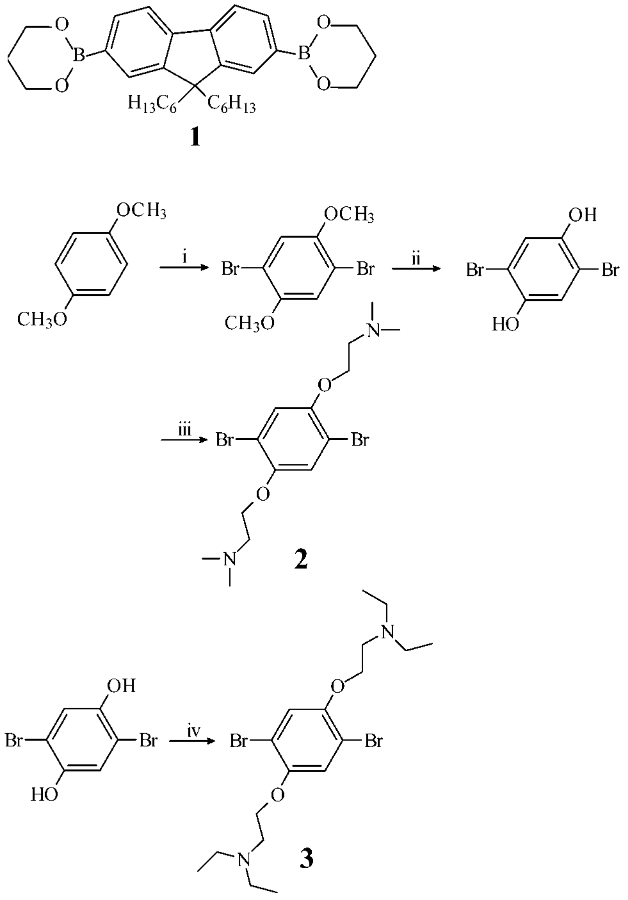
Synthesis. 9,9-Dihexylfluorene-2,7-bis(trimethylene boronate) (**1**),[27] 2,5-bis[3-(*N*,*N*-dimethylamino)-1-oxapropyl]-1,4-dibromobenzene (**2**), 1,4-dibromo-2,5-dimethoxybenzene, and 1,4-dibromohydroquinone were prepared according to the procedures reported in the literature.[11] A detailed synthesis of **P1** and its quaternized salt **P3** was described in our previous report.[28]

2,5-Bis[3-(*N*,*N*-diethylamino)-1-oxapropyl]-1,4-dibromobenzene, 3.[11] A 500 mL round-bottom flask with magnetic spin bar was charged with anhydrous potassium carbonate (72.0 g, 521.0 mmol), 2-(diethylamino)ethyl chloride hydrochloride (22.6 g, 131.0 mmol), and 300 mL of acetone. The stirred mixture was sparged with nitrogen for 15 min followed by the addition of 2,5-dibromohydroquinone (15.0 g, 56.0 mmol). After 15 min of additional sparging, the reaction mixture was brought to reflux for 3 days. Acetone was removed, and the reaction mixture was diluted with 300 mL of water, dissolving all salts. The product was extracted with ether, and the combined organic layer was washed with 10% NaOH(aq) (2 × 100 mL), water (2 × 100 mL), and brine (1 × 100 mL). The solution was dried over $MgSO_4$, filtered, and stripped of solvent by vacuum evaporation to yield crude oily solids. The crude solid was recrystallized from $MeOH/H_2O$ to afford **3** (12.5 g, 48.4%) as white crystals. ^1H NMR (300 MHz, $CDCl_3$, ppm): δ 7.12 (s, 2H), 4.04−3.99 (t, 4H, $J = 6.03$ Hz), 2.92−2.88 (t, 4H, $J = 6.22$ Hz), 2.68−2.61 (q, 8H, $J = 7.09$ Hz), 1.10−1.05 (t, 12 H, $J = 7.21$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 150.25, 118.47, 110.92, 70.01, 51.55, 47.98, 12.10. Anal. Calcd for $C_{18}H_{30}N_2O_2Br_2$: C, 46.37; H, 6.49; N, 6.01; Br, 34.28. Found: C, 46.65; H, 5.99; N, 5.99; Br, 34.32.

Poly[{2,5-bis[3-(*N*,*N*-diethylamino)-1-oxapropyl]-1,4-phenyl}-*co*-alt-2,7-(9,9-dihexylfluorene)], P2. To the mixture of 9,9-dihexylfluorene-2,7-bis(trimethylene boronate) (251 mg, 0.499 mmol), 2,5-bis[3-(*N*,*N*-diethylamino)-1-oxapropyl]-1,4-dibromobenzene (233 mg, 0.500 mmol), tetrabutylammonium chloride (80 mg) and tetrakis(triphenylphosphine) palladium [$Pd(PPh_3)_4$] (10 mg) was added a degassed mixture of 3 mL of toluene ([monomer] = 0.25 M) and 2 mL of 2 M potassium carbonate aqueous solution. The mixture was vigorously stirred at 75 °C for 48 h. After the mixture was cooled to room temperature, it was poured into 200 mL of methanol and deionized water (10:1). A fibrous solid was obtained by filtration. The solid was washed with methanol, water and then methanol. After being washed for 24 h in a Soxhlet apparatus with acetone to remove oligomers and the catalyst residues, the resulting polymer **P2** was obtained (370 mg, 57.1%) as a white fibrous solid. ^1H NMR (300 MHz, $CDCl_3$, ppm): δ 7.80−7.78 (br, 2H), 7.60 (br, 4H), 7.12 (s, 2H), 4.17 (br, 4H, $-OCH_2$), 2.92 (br, 4H, $-CH_2N$), 2.66 (br, 8H, $-NCH_2CH_3$), 2.05 (br, 4H), 1.12−0.78 (br, 34H). ^1H NMR (75 MHz, $CDCl_3$, ppm): δ 150.74, 150.49, 140.02, 137.07, 131.46, 128.31, 124.35, 119.40, 116.92, 68.65, 55.21, 52.08, 47.98, 40.81, 31.90, 30.23, 24.22, 22.91, 14.20, 12.13. FT-IR (KBr, cm^{-1}): 2962, 2927, 2856, 2810, 1509, 1461, 1381, 1203, 1132, 1052, 1035, 888, 870, 822, 753. Anal. Calcd for $C_{43}H_{62}O_2N_2 \cdot H_2O$: C, 80.82; H, 9.84; N, 4.27. Found: C, 79.68; H, 9.79; N, 4.35.

Poly[{2,5-bis[3-(*N*,*N*,*N*-triethylamino)-1-oxapropyl]-1,4-phenyl}-*co*-alt-2,7-(9,9-dihexylfluorene) dibromide], P4 (30% Quaternized). A 100 mL flask with a magnetic spin bar was charged with the polymer **P2** (100 mg) dissolved in 50 mL of THF. Bromoethane (1.09 g, 10.0 mmol) was added to this solution, and the mixture was stirred at room temperature for 24 h. THF and extra bromoethane were evaporated. The polymer was precipitated by the addition of about 100 mL of acetone to the flask, collected by centrifugation, washed with chloroform and acetone, and dried overnight in vacuo at 50 °C. The desired polymer **P4** (72 mg, 66.2%) was obtained as off-white powders. ^1H NMR (300 MHz, $CDCl_3$, ppm): δ 7.80−7.78 (br, 2H), 7.60 (br, 4H), 7.12 (s, 2H), 4.17 (br, 4H, $-OCH_2$), 2.92 (br, 4H, $-CH_2N$), 2.66 (br, 9.2H, $-NCH_2CH_3$), 2.05 (br, 4H), 1.12−0.78 (br, 36H). FT-IR (KBr, cm^{-1}): 2966, 2927 (weak), 2857 (weak), 1509, 1461, 1381, 1202, 1050, 887, 822, 753.

Scheme 1. Synthetic Routes for the Monomers[a]

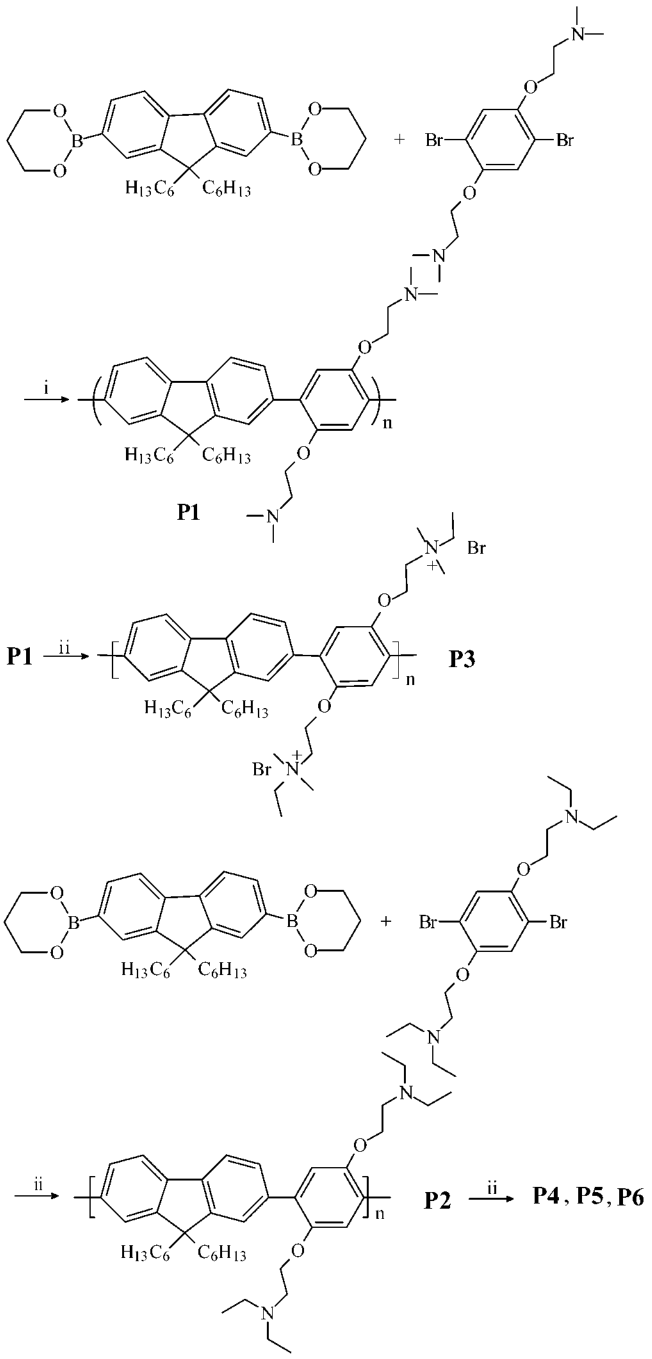


[a] Reagents and conditions: (i) Br_2, CCl_4, RT; (ii) BBr_3, CH_2Cl_2, 0 °C to RT; (iii) K_2CO_3, 2-(dimethylamino)ethyl chloride hydrochloride, acetone, reflux, 3 days; (iv) K_2CO_3, 2-(diethylamino)ethyl chloride hydrochloride, acetone, reflux, 3 days.

Poly[{2,5-bis[3-(*N*,*N*,*N*-triethylamino)-1-oxapropyl]-1,4-phenyl}-*co*-alt-2,7-(9,9-dihexylfluorene) dibromide], P5 (60% Quaternized). A 100 mL flask with a magnetic spin bar was charged with the polymer **P2** (100 mg) dissolved in 50 mL of THF. To this solution was added bromoethane (1.09 g, 10.0 mmol) and 12 mL of DMSO. The solution was stirred at room temperature for 2 days. THF and extra bromoethane were evaporated. The polymer was precipitated by the addition of about 100 mL of acetone to the flask, collected by centrifugation, washed with chloroform, acetone, and dried overnight in vacuo at 50 °C. The desired polymer **P5** (54 mg, 46.2%) was obtained as light pink color powders. ^1H NMR (300 MHz, CD_3OD, ppm): δ 7.80−7.78 (br, 2H), 7.60 (br, 4H), 7.12 (s, 2H), 4.45 (br, 4H, $-OCH_2$), 3.55 (br, 4H, $-CH_2N$), 3.20 (br, 10.4H, $-NCH_2CH_3$), 2.05 (br, 4H), 1.12−0.78 (br, 37H). FT-IR (KBr, cm^{-1}): 2925, 2855, 2629, 2475, 1622, 1511, 1462, 1393, 1202, 1030, 829, 754.

Poly[{2,5-bis[3-(*N*,*N*,*N*-triethylamino)-1-oxapropyl]-1,4-phenyl}-*co*-alt-2,7-(9,9-dihexylfluorene) dibromide], P6 (80% Quaternized). According to the procedure for **P5**, after 100 mg of **P2** was treated with bromoethane in DMSO/THF (1:4) at 50 °C for 5 days, the desired polymer **P6** (62 mg, 50.0%) was obtained as light pink color powders. ^1H NMR (300 MHz, CD_3OD, ppm): δ 7.80−7.78 (br, 2H), 7.60 (br, 4H), 7.12 (s, 2H), 4.45 (br, 4H, $-OCH_2$), 3.55 (br, 4H, $-CH_2N$), 3.20 (br, 11.2H, $-NCH_2CH_3$), 2.05 (br, 4H), 1.12−0.78 (br, 39H). ^{13}C NMR (50 MHz, CD_3OD, ppm): δ 153.66, 152.34, 142.57, 139.42, 134.44, 131.29, 126.10, 121.62, 119.10, 66.87 (64.88 weak), 58.10 (weak), 57.78, 55.91, 53.61, 42.34, 33.93, 31.93, 26.44, 24.76, 15.50, 10.51, 9.03. FT-IR (KBr, cm^{-1}): 2927, 2855, 2622, 2472, 1622, 1511, 1462, 1394, 1202, 1039, 829, 771.

Scheme 2. Synthetic Routes for the Polymers[a]

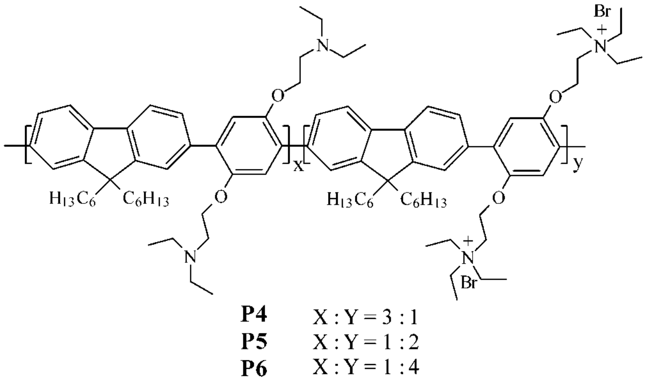


[a] Reagents and conditions: (i) $[(PPh_3)_4]Pd^0$ (1.0 mol %), toluene/2 M K_2CO_3 (3:2), tetrabutylammonium chloride, 75 °C, reflux, 48 h; (ii) C_2H_5Br, DMSO/THF (1:4).

Results and Discussion

Synthesis and Characterization. The general synthetic routes toward the monomers and polymers are outlined in Schemes 1 and 2, respectively. The monomer **1**, 9,9-dihexylfluorene-2,7-bis(trimethylene boronate), was synthesized from 2,7-dibromofluorene.[28] 2,5-Dibromohydroquinone was obtained by the treatment of 1,4-dibromo-2,5-dimethoxybenzene with BBr_3 in dry dichloromethane.[11] As to the monomers **2** and **3**, 2,5-bis[3-(*N*,*N*-dimethylamino)-1-oxapropyl)-1,4-dibromobenzene] and 2,5-bis[3-(*N*,*N*-diethylamino)-1-oxapropyl)-1,4-dibromobenzene] were prepared by reactions between 2,5-dibromohydroquinone and 2-(dimethylamino)ethyl chloride hydrochloride or 2-(diethylamino)ethyl chloride hydrochloride in refluxing acetone in the presence of excess anhydrous potassium carbonate.[12]

The synthesis of the neutral polymers depicted in Scheme 2 is based on the Suzuki coupling reaction, which was carried out in a mixture (3:2 in volume) of toluene and aqueous potassium carbonate solution (2 M) containing 1 mol % $Pd(PPh_3)_4$ under vigorous stirring at 85−90 °C for 48 h in the nitrogen atmosphere. A small amount of tetrabutylammonium chloride was added as the phase transfer catalyst. The obtained polymer was further purified by washing with acetone in a Soxhlet apparatus for 24 h to remove oligomers and catalyst residues and was dried under reduced pressure at room temperature. After purification and drying, the neutral polymers **P1** and **P2** were obtained as white fibrous solids. The terminal groups in the neutral polymers provided the possibility to synthesize water-soluble polymers through the post-polymerization approach. Conversion of the neutral polymers (**P1** and **P2**) to the final water-soluble polymers of **P3** and **P6** was achieved by stirring the neutral polymers with bromoethane in dimethyl sulfoxide (DMSO) and tetrahydrofuran (THF) (1:4) at 50 °C for 5 days. Through adjusting the post-polymerization conditions, the quaternization degree could be controlled, which in turn determined the solubility of the polymers in water. Stirring the neutral polymer **P2** with bromoethane in THF at room temperature for 24 h afforded the polymer **P4** with a quaternization degree of about 30%. Following the same reaction conditions for **P3** and **P6** with less reaction time and lower reaction temperature afforded polymer **P5** with a quaternization degree of about 60%. The quaternization degree was estimated from the respective ^1H NMR spectrum, which will be discussed later.



The post-polymerization approach for the realization of water solubility allows us to characterize the molecular weight at the stage of the neutral polymers, which otherwise is often a problem since polyelectrolytes have a strong tendency to aggregate and adsorb on column fillers. No clear values for molecular weights could otherwise be obtained using conventional techniques.[15] The molecular weights of the neutral polymers were measured by means of gel permeation chromatography (GPC) using THF as the eluant and polystyrene as the standards. The molecular weights of the polymers **P1** and **P2** are satisfactory, with M_w values of 47 000 and 22 100 and M_n values of 29 400 and 17 100, respectively, which are suitable for further post-polymerization.

The obtained neutral polymers **P1** and **P2** readily dissolve in common organic solvents, such as THF, chloroform, toluene, and xylene, but insoluble in DMSO, methanol, and water. With an increased side chain

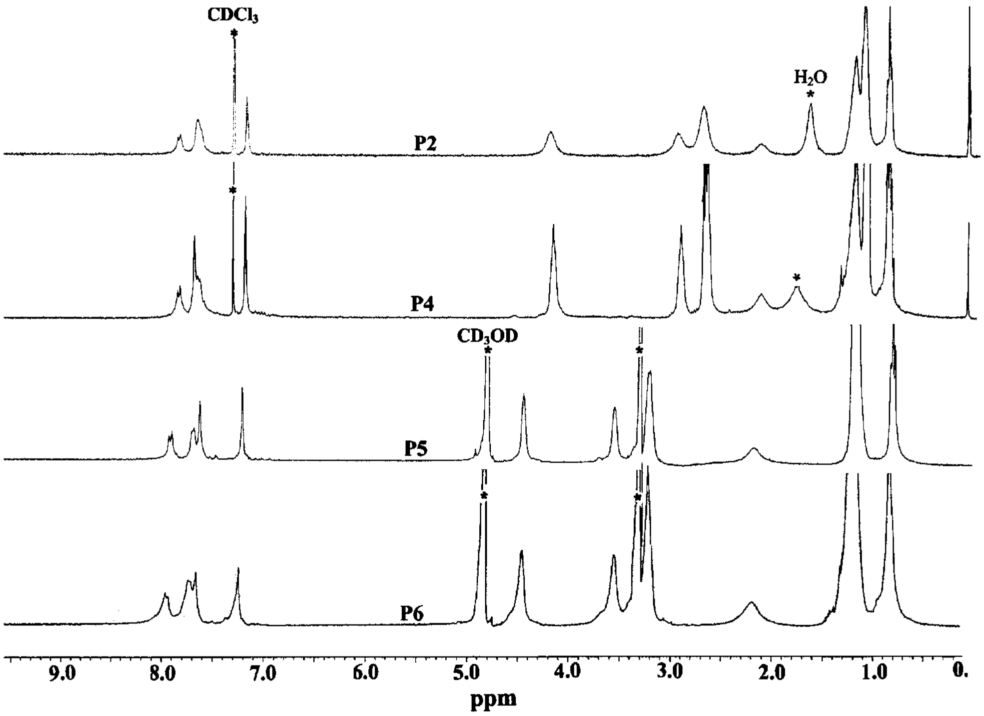


Figure 1. ^{1}H NMR spectra of **P2** and **P4**−**P6**.

length, **P2** has a better solubility than **P1**. After quaternization, the resulting polymer **P3** shows solubility characteristics opposite to that of **P1**, being completely soluble in DMSO, methanol, and water, but insoluble in $CHCl_3$ and THF. Interesting solubility is also found for the polymers with different quaternization degree of **P4**−**P6**. As calculated from the ^{1}H NMR spectrum, **P4**, with a quaternization degree of 30%, has a reduced solubility in THF, chloroform, toluene, and xylene, as compared to the neutral polymer **P2**, while it also has poor solubility in the polar solvents. Ongoing with the increased quaternization degree, the solubility of the polymers in common organic solvents decreased and the solubility in polar solvents, such as DMSO and water, increased gradually. Polymers **P5** and **P6**, with a quaternization degree of 60% and 80% respectively, have very good solubility in DMSO (35 mg/mL for **P6**) and methanol (40 mg/mL for **P6**) as well as satisfactory solubility in water (2 mg/mL for **P6**). Meanwhile, they have shown solubility characteristics opposite to that of **P2**, being completely insoluble in $CHCl_3$ and THF. With the increased quaternization degree, the polymer **P6** has better water solubility as compared to that of **P5**. By control of the quaternization conditions, polymers with different quaternization degrees have been synthesized. However, the reproducibility of the quaternization degree is not very satisfactory.

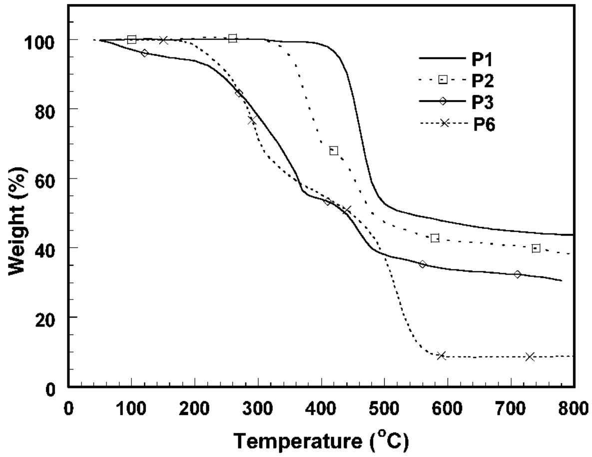


Figure 2. Thermalgravimetric analysis of **P1**−**P3** in a nitrogen atmosphere and **P6** in air.

Figure 1 displays the ^{1}H NMR spectra of the neutral polymer **P2** and its quaternized salts **P4**−**P6**. The well-resolved peaks at δ 4.12, 2.87, and 2.60 ppm, correspond to the methylene groups adjacent to the oxygen ($-OCH_2$) and nitrogen ($-CH_2N$) atoms, and the methyleneamino groups ($-\mathrm{NC}H_2\mathrm{CH}_3$), respectively. The terminal methyl groups ($-\mathrm{NCH_2C}H_3$) appear at around 1.0 ppm, mixing together with the peaks for the hexyl groups attached to the 9-position of the fluorene rings. After treatment with bromoethane, the peaks in the aromatic region remain almost unchanged for all the spectra of **P4**, **P5**, and **P6**. However, for **P5** and **P6**, all of the signals corresponding to the methylene groups in $-OCH_2$, $-CH_2N$, and $-\mathrm{NC}H_2\mathrm{CH}_3$, shift to the lower field of 4.45, 3.55, 3.20, respectively, using methanol-*d* as the solvent. The chemical shifts for the peaks remain unchanged for **P4** (the spectrum was collected using chloroform-*d* as the solvent), only an increased integration ratio for the two peaks of ($-\mathrm{NC}H_2\mathrm{CH}_3$) and ($-CH_2N$) is observed in the spectrum, as compared to the neutral polymer **P2**. The relative integrals of each pair of the ($-\mathrm{NC}H_2\mathrm{CH}_3$) and ($-CH_2N$) can thus be used to estimate the quaternization degree. The calculated quaternization degree for **P4**, **P5**, and **P6** are about 30%, 60%, and 80%, respectively.

The thermal stability of the polymers in nitrogen was evaluated by thermogravimetric analysis (TGA) (**P6** was measured in air). The thermograms are depicted in Figure 2. The neutral polymers, **P1** and **P2**, possess good thermal stability. The onset degradation temperature of **P1** was 400 °C in nitrogen, whereas for **P2** it was 340 °C. However, the quaternized salts began decomposition at ca. 200 °C, with a small amount of water loss at lower temperatures. The first mass loss

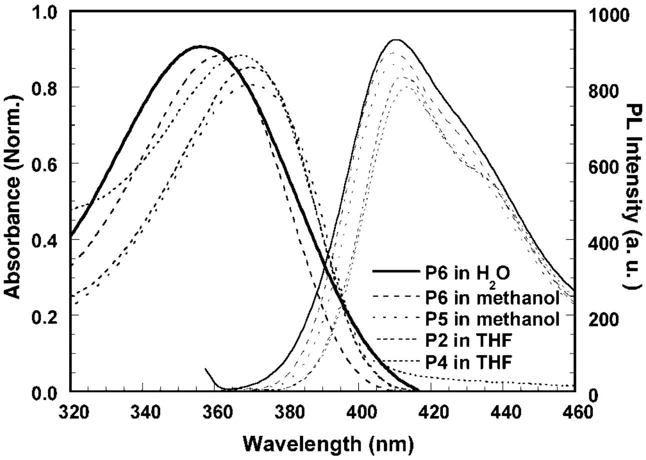


Figure 3. UV−vis absorption and PL emission spectra of **P6** in water, **P6** and **P5** in methanol, and **P2** and **P4** in THF solution.

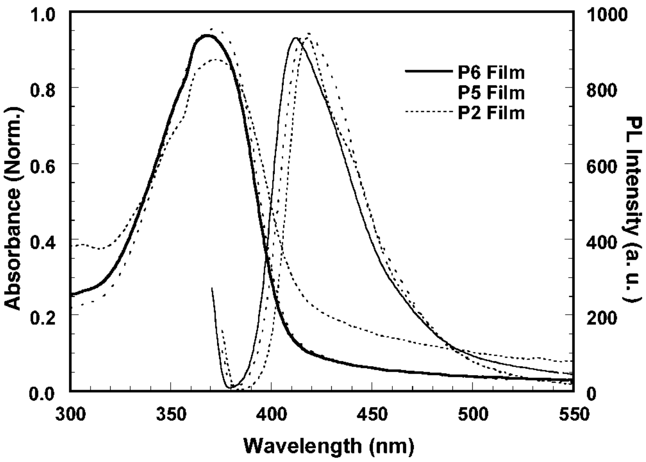


Figure 4. UV−vis absorption and PL spectra of **P2**, **P5**, and **P6** as films.

was from ethyl bromide, as reported by Reynolds et al.[12] A second major transition occurred in the vicinity of the first transition of the neutral polymer, again due to the side chain cleavage. A residual mass, approximately 30% of the starting mass, remained at 800 °C for **P3**. In air, the decomposition temperature was slightly lowered, and there was almost no residue left for **P6** after being heated to 600 °C. These results show that the alkylated polymers could be useful for the preparation of multilayer light-emitting films by electrostatic deposition and that they thermally dealkylate.

Optical Properties. The optical properties of **P1** and its quaternized salt **P3** were reported previously.[29] The spectroscopic properties of **P2** and **P4**−**P6** were measured both in solution and as thin films. The UV−vis absorption and PL spectra of **P2** and **P4** in THF (ca. 1×10^{-5} M) are shown in Figure 3. **P2** exhibied the absorption maximum at 370.5 nm. Its PL spectrum peaked at 414 nm, with a small shoulder at 428 nm. Both the UV and the PL spectra of **P4** are slightly blue shifted as compared to **P2**, with the main absorption peak at 367.5 nm and the emission maximum at 413 nm. It is also found that the absorption spectrum for **P4** is broadened as compared to that of **P2**, an indication of some aggregation formation, which is due to the limited solubility of **P4** in THF as compared to that of **P2**. Comparison of the electronic spectra of the quaternized salt **P6** in methanol with the neutral polymer **P2** in THF could find a slight blue shift in both the absorption and the emission spectra for **P6**. The difference might be attributed to the quaternization, and the mutual repulsion of positive charges led to an increased torsion angle along the polymer main chain. With the increased quaternization degree, the UV spectrum of **P6** was obviously blue shifted as compared to **P5**, due to the increased repulsion among the positive charges. It is possible that, for the alkylated polymer in a polar medium of low ionic strength, the mutual repulsion of positive charges housed on alternate rings leads to a lowest energy conformation where the torsional angle is increased. This is analogous to the argument made for the chain extension observed with flexible polyelectrolytes under similar conditions, namely the polyelectrolyte effect.[12] The absorption peak of **P6** in methanol occurred at 360.5 nm, and its emission peaked at 410 nm. A slight blue shift was observed for the absorption spectra between the polymer **P6** measured in water and methanol. The electronic spectra were dependent on the solvents, showing a bathochromic shift with a decrease in the solvent polarity, just similar to the properties of **P3**, which has been studied in details before.[29] The corresponding UV and PL spectra are also shown in Figure 3.

Transparent and uniform films of the water-soluble polymers **P5** and **P6** were prepared on quartz plates by spin-casting their methanol solutions at room temperature. The films of **P5** and **P6** emitted intense blue light by the excitation of UV light. The UV−vis and PL spectra of **P5** and **P6** as films are displayed in Figure 4. Slight blue shifts were also observed among the UV and PL spectra of **P6**, **P5**, and **P2**. Similar to the effect of the sulfonate end group to the conformational change of thiophene studied by Holdcroft et al.,[30] the presence of ammonium salts attached to the terminus of the alkyl side chain on the derivatized phenylene rings may prevent the polymer chains from achieving a higher degree of coplanarity and π-conjugation in the solid state. Another factor of ion aggregation may also be considered, since it is believed that ion aggregation is more pronounced for polymers containing large concentrations of covalently bound ions.[30] For **P5** and **P6**, which are polyelectrolytes containing one ionic species almost every two repeating units, ion aggregation is expected to occur in the solid state.

From the application point of view, one of the most attractive properties of the polymers is the relatively high PL quantum yield (Φ_{pl}). Both the neutral polymer and the quaternarized polymers displayed strong blue fluorescence either in solutions or as films upon exposure to UV light. The Φ_{fl} of the neutral polymer (**P1**) was as high as 87% when measured from its dilute solution in chloroform, while a PL quantum efficiency of 57% was observed for **P2** in its THF solution, using the quinine sulfate solution (ca. 1.0×10^{-5} M) in 0.10 M H_2SO_4 (quantum yield, 55%) as a standard.[31] For polymer **P3** (with a 80% quaternization degree), the Φ_{pl} was measured to be 76% from its dilute solution in methanol. When the measurement was conducted in aqueous solution, the corresponding value of Φ_{pl} was 25%. The decreased PL efficiency may be attributed to the aggregation of the polymer in aqueous solution. This was supported by a further reduced PL efficiency measured in the solid state (films on quartz plate cast from methanol solution), which was 4% compared with 9,10-diphenylanthracene as standard (dispersed in PMMA films with a concentration lower than 1×10^{-3}

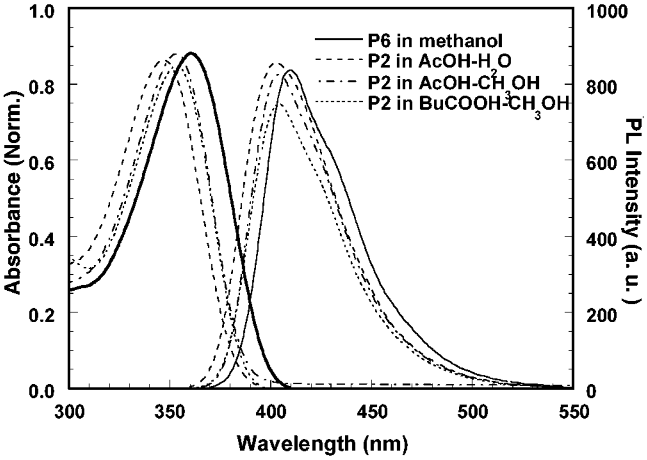


Figure 5. UV−vis absorption and PL emission spectra of **P2** in different organic acids, as compared to the spectra of **P6** in methanol.

M, assuming a PL efficiency of 83%).[32] **P6** had similar PL efficiencies as those for **P3**.

Acid-Assisted Water Solubility of P2. The properties of a neutral polymer can be examined in both aqueous and nonaqueous media. As reported by Reynolds et al.,[12] the neutral polymers with the same amino functional group attached on the phenylene ring were soluble in many organic solvents and aqueous acids through protonation but were insoluble in neutral water. It is interesting to find that **P2** had different solubilities in aqueous acids. **P2** had poor solubility in 1 M HCl aqueous or methanol solution, while it dissolved very well in either the 1 M acetic acid aqueous solution or the acetic acid−methanol solution. Solubility of **P2** in acetic acid aqueous solution was even better than that of the polymer **P6** in water. Comparison of the UV and PL spectra of **P6** in methanol and those of **P2** in different aqueous acid or acid−methanol solutions is shown in Figure 5. It is obvious that blue shifts for both the absorption and emission were observed for **P2** in organic acids as compared to **P6** in methanol. However, similar absorption and emission spectra were observed for **P2** in acetic acid−methanol and butyric acid−methanol solution, with the absorption maximum at 353 nm and an emission peak at 404 nm. The absorption maximum of the **P2**−acetic acid aqueous solution was at 345 nm, which was blue shifted about 8 nm as compared to its acetic acid methanol solution, while a blue shift of about 15 nm was observed as compared to **P6** in methanol. However, the emission spectrum of **P2** in acetic acid aqueous solution (402 nm) was only slightly blue shifted as compared to its acetic acid methanol solution. (404 nm).

Detailed study has found that **P2** could not be dissolved in aqueous solutions of strong acids, such as sulfuric acid and *p*-toluenesulfonic acid. However, even a few drops of acetic acid in water or methanol could dissolve **P2** very well. The increased solubility of the polymer in polar organic solvents is probably contributed to the interaction between the weak organic acid and the terminal amino groups through the electrostatic interaction that could increase the affinity of the polymer with those polar solvents. With the increased chain length of the aliphatic organic acid, the solubility of **P2** in aqueous acid decreased. **P2** can only be dissolved in the *n*-butyric acid−methanol solution but not in the *n*-butyric acid−aqueous solution. It is easy to understand that with the increased chain length of the aliphatic acid, the overall nonpolar components of the resultant polymers increased, which led to better solubility in methanol than in water. This is similar to the observations for the quaternized salt of **P2**, a higher quaternization degree of the polymer will lead to a better solubility in the more polar solvent, such as **P6** exhibited a better water solubility than **P5**, since the positively charged terminal group is polar. In addition to the modulation of the water solubility to the PF derivatives through the tuning of the electrostatically attached substituents, various functional substituents could be easily attached to the PF backbone combining the inherent chromic properties of the latter species with the affinity and/or recognition properties of adequately selected substituents, opening the way to the fabrication of solid-state recognition/affinity sensors.[5b]

The unusual solubility of **P2** in acetic acid aqueous solution has driven us to study the interaction between the acid and the neutral polymer **P2**. It is normally accepted that a quaternization salt could be formed in the acetic acid aqueous solution, which upon separation should have a good solubility in methanol or water. However, it was found that if the **P2**−acetic acid methanol solution was poured into hexane, the resulting precipitate (**P2′**) could not be dissolved in either water or methanol but had a good solubility in chloroform and THF, with solubility properties similar to those of the neutral polymer **P2**. It is possible that in contradiction to the normally accepted protonation of the terminal nitrogen atoms, only a weak interaction was formed between the nitrogen atoms and the acetic acid in aqueous solution. This assumption was confirmed by the same electronic spectra between **P2** and the recovered polymer (**P2′**) in THF solution. In addition, comparison of the ^{1}H NMR spectra between the recovered polymer (**P2′**) in chloroform-*d* and the **P2** in chloroform-*d* with one drop of acetic acid (**P2″**) had clearly demonstrated that there was some interaction, but not bond formation between the nitrogen atoms and the acetic acid. As depicted in Figure 6, the ^{1}H NMR spectra of **P2** and the recovered polymer (**P2′**) were exactly the same, indicative of the same structure. However, for the ^{1}H NMR spectrum of the polymer **P2** with one drop of acetic acid, all of the signals corresponding to the methylene groups in $-OCH_2$, $-CH_2N$, and $-NCH_2CH_3$ shifted to the lower field to be 4.40, 3.45, and 3.10, respectively, indicative of some kind of weak interaction existed. The chemical shifts of these characteristic peaks are similar to those of **P6**, which has a quaternization degree of about 80%. This unusual property is of special interest in the device fabrication, since the neutral polymers have good solubility in water with several drops of acetic acid, which recovers upon thermal treatment under vacuum. The generality of the acid−base interaction between the functional amines and the organic acids also opens the way to a novel area of surface modification through the use of electrostatic interactions.

Electrochemical Properties. The electrochemical behavior of the polymers **P2**, **P5**, and **P6** was investigated by the cyclic voltammetry (CV). The CV was performed in a solution of Bu_4NClO_4 (0.10 M) in acetonitrile at a scan rate of 50 mV/s at room temperature under the protection of argon. A platinum electrode (~0.08 cm^2) was coated with a thin polymer film

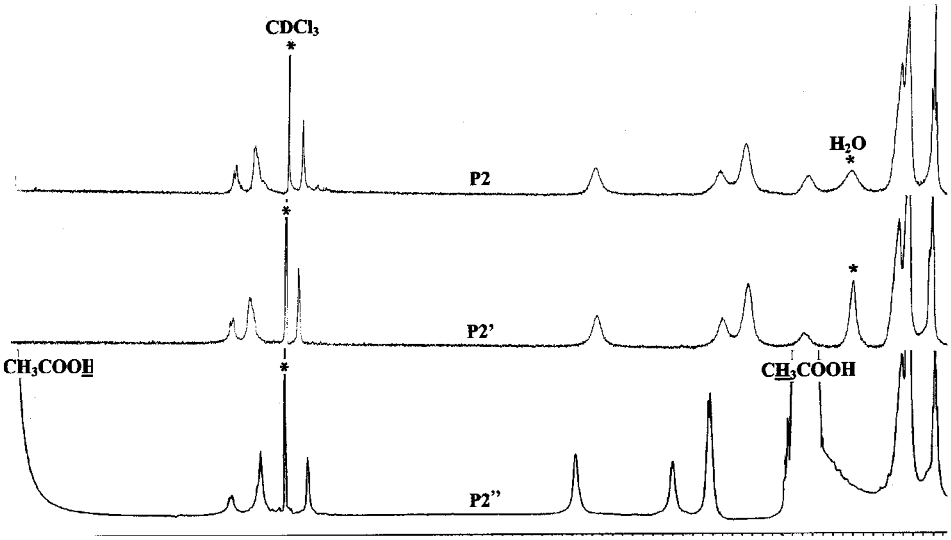


Figure 6. Comparison of the ^{1}H NMR spectra among **P2**, recovered **P2′** and **P2** with a drop of acetic acid (**P2″**).

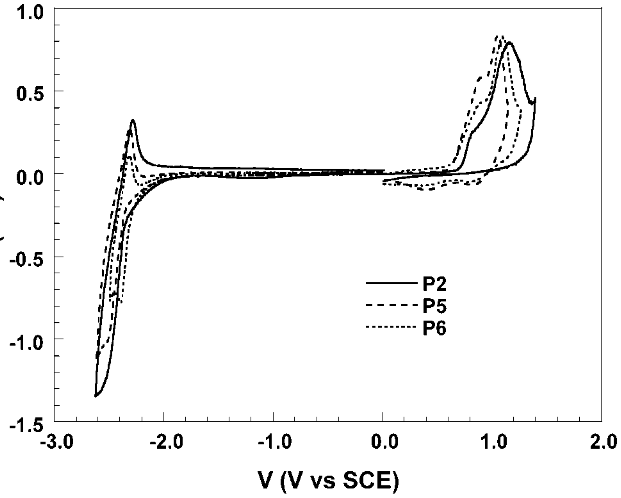


Figure 7. Cyclic voltammograms of **P2, P5**, and **P6** films coated on platinum plate electrodes in acetonitrile containing 0.1 M Bu_4NClO_4. Counter electrode: platinum wire. Reference electrode: $Ag/AgNO_3$ (0.10 M in acetonitrile). Scan rate: 50 mV/s.

and was used as the working electrode. A Pt wire was used as the counter electrode, and an $Ag/AgNO_3$ electrode was used as the reference electrode.

Comparison of the cyclic voltammograms among polymers **P2**, **P5**, and **P6** are shown in Figure 7. All of the three polymers exhibited partial reversibility in the n-doping process and almost nonreversibility in p-doping processes. For the neutral polymer **P2**, during the anodic scan, the polymer exhibited an irreversible two-electron oxidation process, with the two anodic peaks at 0.86 and 1.16 V, respectively. While for the quaternized polymers either with a quaternization degree of 60% (**P5**) or 80% (**P6**), a similar shape of the CV curves with improved reversibility as compared to the neutral polymer of **P2** was observed for these two polymers. The improved reversibility is reasonable: during the oxidation, the counterions will diffuse from the bulk electrolyte solution to the oxidation site to balance the charges. The quaternized salt will help to overcome the difficulties for the counterions to migrate. Another reason is that the charge transport from the polymer to the electrode (or vice versa) might be much easier for the quaternized polymers.

For the three polymers, the first oxidation peak occurred at around 0.9 V, which might be attributed to the oxidation of the terminal amino groups.[33] For the polymer **P2**, the second oxidation peak occurred at 1.05 V, which is due to the oxidation of the main chain structure. As we studied before, the oxidation potential (at 1.05 V) is very similar to that of the polymers having the same backbone structure and substitutions on the fluorene unit, but without the terminal amino groups in the polymer side chain.[34] The oxidation potential for the main chain of the quaternized polymers (**P5** and **P6**) were similar, which was slightly decreased by 0.1 V as compared to that of the neutral polymer (**P2**). The reduction potentials and the shapes of the curves were similar for the three polymers, which implied that the reduction properties of the polymers were dominated by the main chain structure. The reduction peak potentials were measured to be − 2.53 V, with the reoxidation peaks at around − 2.32 V. For **P5**, the n-doping processes could be run up to 20 cycles without any obvious change in the shape of the CV. However, the current intensity showed a slow trend to decrease.

Conclusions

In summary, we have synthesized a series of new cationic water-soluble conjugated polymers based on the alternating fluorene and phenylene backbone structure through a facile post-polymerization approach, which permits a full structural characterization and the control of the cationic degree. It was found that the polymers of different quaternization degree had shown different solubilities in common organic solvents. Better solubility in polar solvents and the spectral blue shift was observed with the polymers with a higher quaternization degree. The optical feature seems related to the conformational change of the conjugated main chain driven by the increased repulsion among the positively charged end groups. In addition, it was found that the neutral polymer had very good water solubility when a few drops of acetic acid were added. The ^{1}H NMR spectra and the optical properties study have demonstrated that instead of forming the normally accepted quaternized salt, only a weak interaction was formed between the electron pair on the N atoms and acetic acid. Better water solubility for the neutral polymer observed in acetic acid aqueous solution rather than in the butyric acid aqueous solution could be attributed to the increased nonpolar components of the resultant polymers. Good thermal stability and intense blue light emission, as well as partially reversible electrochemical properties, have been demonstrated for this series of polymers. The tunable water solubility and high fluorescence quantum yields make them attractive materials for the application in organic LED devices and as fluorescent biosensors.

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