Synthesis and Light Emitting Properties of Polyacetylenes Having Pendent Fluorene Groups

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ABSTRACT: Five novel fluorene-containing polymers, poly[(9,9-dimethylfluoren-2-yl)acetylene] (PFA1), poly[1-pentyl-2-(9,9-dimethylfluoren-2-yl)acetylene] (PFA2), poly[1-decyl-2-(9,9-dimethylfluoren-2-yl)acetylene] (PFA3), poly[1-phenyl-2-(9,9-dimethylfluoren-2-yl)acetylene] (PFA4), and poly[1-(3,4-difluorophenyl)-2-(9,9-dimethylfluoren-2-yl)acetylene] (PFA5) were synthesized by the polymerization of the corresponding fluorene-substituted acetylenic monomers (M1–M5), using WCl6, MoCl5, and TaCl5 as catalysts and n-Bu4Sn as a cocatalyst. The synthesized polymers were thermally stable and readily soluble in common organic solvents. The degradation temperatures for a 5% weight loss of the polymers were ~352–503 °C under nitrogen. PFA1–PFA5 show emission peaks from 402 to 590 nm. Besides, their electroluminescent properties were studied in heterostructure light-emitting diodes (LEDs), using PFA2–PFA5 as an emitting layer. The PFA5 device revealed an orange-red emission peak at 602 nm with a maximum luminescence of 923 cd/m² at 8 V. A device with the ITO/PEDOT/a mixture of PFA2 (98 wt %) and PFA5 (2 wt %)/Ca/Al showed near white emission. Its maximum luminance and current efficiency are 450 cd/m² at 15 V and 1.3 cd/A, respectively. © 2005 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 44: 519–531, 2006

Keywords: fluorescence; light-emitting diodes (LED); photoluminescence; polyacetylene

INTRODUCTION

Conjugated polymers have been extensively studied for their potential applications in light emitting diodes, organic lasers, thin film transistors, and solar cells. Polyacetylene is a prototypical conjugated polymer among many promising conjugated polymers, which exhibits high conductivity upon doping. The conductivities of this polymer can reach as high as 10⁵ S/cm. Although polyacetylene shows a very high electrical conductivity by doping, this polymer has rarely been used as a light-emitting polymer for electroluminescent (EL) devices because nonsubstituted polyacetylene is insoluble, infusable, and unstable in air and exhibits almost no photoluminescence (PL) in the visible region.

Substituted polyacetylenes such as poly(phenylacetylene) (PPA) were reported by Percec and coworkers. Recently, Masuda and coworkers, Tang and coworkers, and our laboratory have also synthesized several series of substituted polyacetylene derivatives, which were stable in air and soluble in common organic solvents. Although the conductivities of these polyacetylene derivatives are not as high as those of nonsubstituted ones, some show both PL and EL properties in the visible wavelength region. The most commonly used substituents for these polyacetylene derivatives are the alkyl and phenyl groups. These alkyl or phenyl-substituted polyacetylenes can emit red to blue light based on different substituents. In general, the PL efficien-
cies of disubstituted polyacetylenes are higher than those of monosubstituted polyacetylenes. The EL efficiencies of these substituted polyacetylenes are rather low. The best EL device using poly[1-(p-butylphenyl)-2-phenylacetylene] doped with 2-(4-biphenyl)-5-(4-t-butylphenyl)-1,3,4-oxadiazole as emitting materials was reported. Its quantum yield, current efficiency, and luminescence were 0.1%, 0.038 cd/A, and 30 cd/m², respectively.

Recently, a naphthalene, a silole, or a carbazole pendant was incorporated into a poly(1-phenyl-1-alkyne) structure by Tang and coworkers. They found that the materials not only exhibited a higher thermal stability, but also emitted a strong blue light. They showed much higher quantum efficiencies than those of alkyl- and phenyl- substituted polyacetylenes. For example, an EL device with the configuration of ITO/poly[1-phenyl-5-[(a-naphthoxy)pentyne]: PVK/bathocuproine/Alq3/LiF/Al, emitted blue light of 468 nm with a maximum brightness of 955 cd/m² and a power efficiency of 0.18 lm/W. Sanda et al. also reported some polyacetylenes with pendant carbazole groups.

The polymers containing fluorene moieties in the main chain or side-chain have attracted considerable attention because of their unique properties of EL applications. Recent examples of the polymers containing pendant fluorene moieties include poly(vinylfluorene), poly(4H-fluorenylacetylene), and poly(4H-fluorenylphenylene vinylene). The bulky fluorene pendant also affects the polymer packing and reduces chain interaction between the polymer backbones. This will improve the performance of polymer light emitting diodes (PLED). In this paper, we incorporated a fluorene unit into the polyacetylene backbones, and investigated their peculiar PL and EL properties.

EXPERIMENTAL

Materials

Bis(triphenylphosphine)palladium(II) chloride (PdCl₂(PPh₃)₂, 99.99%), copper(I) iodide (CuI, 98%), triphenylphosphine (PPh₃, 99%), 2-methyl-3-butyln-2-ol (98%), tetra-n-butyltin (n-Bu₄Sn), molybdenum(V) chloride (MoCl₅, 99.9%), and tantalum(V) chloride (TaCl₅, 99.99%) were purchased from Aldrich. Tungsten(VI) chloride (WCl₆) was purchased from ACROS. All commercial products were used without further purification. Tetrahydrofuran (THF) was dried over sodium, and dioxane, triethylamine (Et₃N), and N,N-dimethylformamide (DMF) were dried over calcium hydride and then distilled under nitrogen.

Techniques

¹H and ¹³C NMR spectra (300 MHz) were recorded on a Varian VXR-300 spectrometer. Fourier transform infrared (FTIR) spectra were recorded as KBr pellets on Perkin Elmer Spectra 1 spectrometer. Mass spectra were obtained on a JEOL JMS-SX 102A mass spectrometer. Thermal transitions and thermodynamic parameters were determined by using a Perkin Elmer Pyris 1 differential scanning calorimeter equipped with a liquid-nitrogen cooling accessory. Heating and cooling rates were 10 °C/min. Gel permeation chromatography (GPC) was run on a Waters 510 LC instrument equipped with a 410 differential refractometer, a UV detector, and a set of polystyrene gel columns of 10², 5 × 10², 10³, and 10⁴ Å. The oven temperature was set at 40 °C. THF was used as eluent and the flow rate was 1 mL/min. The UV–visible spectra and photoluminescence spectra of polymers were measured from an HP 8453 diode-array spectrophotometer and a Hitachi F-4500 luminescence spectrophotometer, respectively. The PL quantum yield (φp) in chloroform solution was measured by integrated sphere. Meanwhile, cyclic voltammetric (CV) measurements were made in acetonitrile (CH₃CN) with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte at a scan rate of 50 mV/s. Platinum wires were used as both the counter and working electrodes, and silver/silver ions (Ag in 0.1 M AgNO₃ solution, from Bioanalytical Systems, Inc.) were used as the reference electrode. The PLED characterization was carried out by a Keithley 2400 source-measure unit and a calibrated silicon photodiode. The brightness was further measured using a Photo Research PR650 spectrophotometer.

Synthesis of Monomers M1–M5

The synthesis of fluorine-substituted acetylenic monomers M1–M5 is outlined in Scheme 1.
2-Iodofluorene (1)

Fluorene (30.0 g, 180 mmol), iodine (23.0 g, 91 mmol), and iodic acid (HIO₃) (8.0 g, 45 mmol) were dissolved in 80% acetic acid aqueous solution containing a small amount of sulfuric acid. The reaction mixture was heated at 80 °C for 4 h under nitrogen atmosphere. After the solution was cooled, the solvent was removed by decantation. The product was washed with methanol and dried to yield 31.6 g (60%) of brown solid; mp: 130–132 °C.

**1H NMR** (300 MHz, CDCl₃) δ (ppm): 3.81 (d, J = 15.9 Hz, 2H), 7.31 (m, 2H), 7.44 (m, 2H), 7.66 (d, J = 7.2 Hz, 1H), 7.73 (d, J = 7.2 Hz, 1H), 7.85 (s, 1H).

**13C NMR** (75 MHz, CDCl₃) δ (ppm): 36.6, 92.5, 120.2, 121.7, 122.3, 127.1, 127.8, 132.2,

_Scheme 1._ Synthesis of monomers M1–M5 and polymers PFA1–PFA5.
9,9-Dimethyl-2-iodofluorene (2)

2-Iodofluorene (25.0 g, 85.6 mmol) was dissolved in THF and treated with potassium tert-butoxide (21.8 g, 0.19 mol) to give a red solution, followed by methylation with methyl iodide (28.2 g, 0.19 mol) at room temperature for 3 h. The product was purified by column chromatography (silica gel, n-hexane as eluent, and Rf 0.7) to yield 25.2 g (92%) of yellow solid; mp: 63–65 °C.

1H NMR (300 MHz, CDCl3) δ (ppm): 1.47 (s, 6H), 7.31 (m, 2H), 7.44 (m, 2H), 7.66 (d, J = 7.2 Hz, 1H), 7.73 (d, J = 7.2 Hz, 1H), 7.85 (s, 1H).

13C NMR (75 MHz, CDCl3) δ (ppm): 26.9, 47.1, 92.5, 120.0, 121.7, 122.5, 127.1, 127.8, 132.0, 135.9, 138.0, 138.6, 153.0, 154.9. MS [M+]+ calcd. for C15H13I 320.17, found 320. ELEM. ANAL. Calcd. for C15H13I: C, 56.27; H, 4.09; I, 39.64. Found: C, 56.21; H, 4.12.

9,9-Dimethyl-2-(3-hydroxy-3-methyl-1-butyl)fluorene (3)

9,9-Dimethyl-2-iodofluorene (25.0 g, 78.1 mmol), PdCl2(PPh3)2 (0.56 g, 0.78 mmol), CuI (1.53 g, 5.86 mmol), and PPh3 (0.74 g, 3.9 mmol) were dissolved in Et3N (250 mL), and the mixture was stirred under nitrogen. After all the catalysts were dissolved, 2-methyl-3-butyn-2-ol (7.88 g, 93.7 mmol) was added. The resulting solution was heated at 70 °C for 12 h. After Et3N was removed under reduced pressure, the product was extracted with diethyl ether. The crude product was isolated by evaporating the solvent and purified by column chromatography (silica gel, ethyl acetate: n-hexane = 1:5 as eluent, and Rf 0.4) to yield 13.0 g (68%) of brown oil.

1H NMR (300 MHz, CDCl3) δ (ppm): 1.47 (s, 6H), 1.65 (s, 6H), 7.31 (m, 2H), 7.41 (m, 2H), 7.48 (s, 1H), 7.66 (m, 2H). 13C NMR (75 MHz, CDCl3) δ (ppm): 26.9, 31.4, 46.8, 66.7, 81.2, 90.4, 119.8, 120.3, 122.5, 122.6, 126.4, 127.0, 127.8, 131.2, 132.0, 138.2, 140.0, 153.9, 154.0. MS [M+]+ calcd. for C20H20O 276.38, found 276. ELEM. ANAL. Calcd. for C20H20O: C, 89.92; H, 7.29; O, 5.79. Found: C, 89.94; H, 7.23.

1-(9,9-Dimethylfluorene-2-yl)acetylene (M1)

9,9-Dimethyl-2-(3-hydroxy-3-methyl-1-butyl)fluorene (10.0 g, 36 mmol) and KOH (4.44 g, 79.2 mmol) were dissolved in dioxane (300 mL). The mixture was heated at 120 °C for 4 h, cooled to room temperature, and 6 N HCl aqueous solution (12 mL) was added. The resulting solution was extracted with ethyl ether. The crude product was isolated by evaporating the solvent and purified by column chromatography (silica gel, n-hexane as eluent, Rf 0.7) to yield 5.8 g (74%) of colorless oil.

1H NMR (300 MHz, CDCl3) δ (ppm): 1.47 (s, 6H), 3.12 (s, 1H), 7.32 (m, 2H), 7.44 (m, 2H), 7.56 (s, 1H), 7.64 (d, J = 7.2 Hz, 1H), 7.67 (d, J = 7.2 Hz, 1H). 13C NMR (75 MHz, CDCl3) δ (ppm): 26.9, 46.8, 77.0, 84.4, 119.8, 120.3, 122.5, 122.6, 126.4, 127.0, 127.8, 131.2, 138.2, 140.0, 153.9, 154.0. MS [M+]+ calcd. for C17H14I 218.30, found 218. ELEM. ANAL. Calcd. for C17H14: C, 93.54; H, 6.46. Found: C, 93.53; H, 6.47.

1-Pentyl-2-(9,9-dimethylfluoren-2-yl)acetylene (M2), 1-Decyl-2-(9,9-dimethylfluoren-2-yl)acetylene (M3), 1-Phenyl-2-(9,9-dimethylfluoren-2-yl)acetylene (M4), and 1-(3,4-Difluorophenyl)-2-(9,9-dimethylfluoren-2-yl)acetylene (M5)

Monomers M2–M5 were synthesized by a similar method. The preparation of monomer M2 is described here. 9,9-Dimethyl-2-iodofluorene (10 g, 31.2 mmol), PdCl2(PPh3)2 (0.22 g, 0.31 mmol), CuI (0.62 g, 2.37 mmol), and PPh3 (0.24 g, 1.26 mmol) were dissolved in Et3N (100 mL), and the mixture was stirred at room temperature under nitrogen. After all catalysts were dissolved, 2-methyl-3-butyn-2-ol (7.88 g, 93.7 mmol) was added. The resulting solution was heated at 70 °C for 12 h. After Et3N was removed under reduced pressure, the product was extracted with diethyl ether. The crude product was isolated by evaporating the solvent and purified by column chromatography (silica gel, n-hexane as eluent, Rf 0.4) to yield 13.0 g (68%) of brown oil.

1H NMR (300 MHz, CDCl3) δ (ppm): 0.93 (t, 3H), 1.48 (s, 6H), 1.62 (s, 6H), 1.65 (s, 6H), 7.31 (m, 2H), 7.41 (m, 2H), 7.48 (s, 1H), 7.66 (m, 2H). 13C NMR (75 MHz, CDCl3) δ (ppm): 26.9, 31.4, 46.8, 66.7, 81.2, 90.4, 119.8, 120.3, 122.5, 122.6, 126.4, 127.0, 127.8, 131.2, 132.0, 138.2, 140.0, 153.9, 154.0. MS [M+]+ calcd. for C22H24O 276.38, found 276. ELEM. ANAL. Calcd. for C22H24O: C, 89.94; H, 7.23; O, 5.79. Found: C, 89.94; H, 7.23; O, 5.79.
Polymerization of Monomers M1–M5

Polymerizations were carried out under nitrogen using either an inert atmosphere glove box or a Schlenk tube in a vacuum line system, except for the purification of the polymers, which was done in open air. A detailed procedure for the polymerization of monomer M1 is given here.

Monomer M1 (0.9 g, 4.12 mmol) was added into a Schlenk tube with a three-way stopcock on the sidearm. The tube was evacuated under vacuum and then flushed with nitrogen three times through the sidearm. Toluene (10 mL) was injected into the tube through a septum to dissolve the monomer. The initiator solution was prepared in another tube by dissolving WCl6 (0.158 g, 0.4 mmol) and n-Bu4Sn (0.28 mg, 0.8 mmol) in 10 mL of dried toluene. Both tubes were aged at room temperature for 30 min. The solution was then cooled to room temperature, diluted with 2 mL of THF, and added drop-wise through a cotton filter to 300 mL of methanol with stirring. The polymer was separated by filtration, purified by several reprecipitations from THF into methanol, and dried in vacuum to yield 0.61 g (68%) of PFA1.

PFA2

Yield: 31%. 1H NMR (300 MHz, CDCl3) δ (ppm): 0.93 (t, 3H), 1.47 (br, 12H), 2.18 (t, 2H), 7.17 (br, 5H), 7.62 (br, 2H). 13C NMR (75 MHz, CDCl3) δ (ppm): 14.0, 19.4, 26.9, 28.5, 31.1, 45.7, 119.7, 120.1, 122.5, 122.6, 125.8, 127.0, 127.3, 130.5, 138.5, 138.6, 140.0, 153.4, 153.7. ELEM. ANAL. Calcd. for C23H16F2: C, 83.62; H, 4.88. Found: C, 83.60; H, 4.91.

PFA3

Yield: 36%. 1H NMR (300 MHz, CDCl3) δ (ppm): 0.93 (t, 3H), 1.27–1.55 (br, 22H), 2.20 (t, 2H), 7.32 (br, 5H), 7.6 (br, 2H). 13C NMR (75 MHz, CDCl3) δ (ppm): 14.1, 19.4, 22.6, 26.9, 28.8, 29.0, 29.2, 29.3, 29.5, 29.6, 31.9, 146.5, 153.4, 153.7. ELEM. ANAL. Calcd. for C23H16F2: C, 83.62; H, 4.88. Found: C, 83.60; H, 4.91.
Table 1. Polymerization of Fluorene-Containing Monomers M1–M5  

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Cat.</th>
<th>Temp. (°C)</th>
<th>Yield (%)</th>
<th>(M_n) b</th>
<th>PDI</th>
<th>(T_g) (°C)</th>
<th>(T_d) (°C) c</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>WCl(_6)</td>
<td>30</td>
<td>68.2</td>
<td>40,500</td>
<td>1.88</td>
<td>76.4</td>
<td>372</td>
</tr>
<tr>
<td>M1</td>
<td>MoCl(_5)</td>
<td>30</td>
<td>57.6</td>
<td>35,000</td>
<td>1.52</td>
<td>76.0</td>
<td>371</td>
</tr>
<tr>
<td>M2</td>
<td>TaCl(_5)</td>
<td>80</td>
<td>30.9</td>
<td>7500</td>
<td>1.35</td>
<td>75.7</td>
<td>377</td>
</tr>
<tr>
<td>M3</td>
<td>TaCl(_5)</td>
<td>80</td>
<td>36.0</td>
<td>8900</td>
<td>1.45</td>
<td>76.3</td>
<td>387</td>
</tr>
<tr>
<td>M4</td>
<td>TaCl(_5)</td>
<td>80</td>
<td>75.3</td>
<td>315,700</td>
<td>3.12</td>
<td>81.5</td>
<td>462</td>
</tr>
<tr>
<td>M5</td>
<td>TaCl(_5)</td>
<td>80</td>
<td>69.2</td>
<td>285,100</td>
<td>2.88</td>
<td>84.4</td>
<td>503</td>
</tr>
</tbody>
</table>

\(a\) All polymerization took place under nitrogen for 24 h in toluene solution and used \(n\)-Bu\(_4\)Sn as cocatalyst. [M] = 0.2M, [WCl\(_6\)] = [MoCl\(_5\)] = [TaCl\(_5\)] = 20 mM, [\(n\)-Bu\(_4\)Sn] = 40 mM.

\(b\) Determined by GPC relative to polystyrene.

\(c\) Temperature of 5% weight loss measured by TGA in nitrogen.

PFA4

Yield: 75%. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm): 1.58 (s, 6H), 7.40 (br, 6H), 7.55 (br, 4H), 7.70 (br, 2H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) (ppm): 26.9, 46.8, 119.9, 120.3, 121.9, 122.5, 122.6, 123.0, 126.0, 127.0, 127.1, 127.7, 128.1, 128.3, 130.7, 131.6, 138.2, 139.4, 153.9, 153.0, 156.4. Elem. Anal. Calcd. for C\(_{23}\)H\(_{18}\): C, 93.84; H, 6.16. Found: C, 92.20; H, 5.89.

PFA5

Yield: 70%. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm): 1.58 (s, 6H), 7.15 (br, 1H), 7.35 (br, 3H), 7.50 (br, 3H), 7.68 (br, 3H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) (ppm): 26.9, 46.8, 117.5 (d), 119.9, 120.3, 120.4 (d), 121.0, 122.5, 122.6, 126.0, 127.1, 127.8, 128.0 (d), 128.1 (d), 130.7, 138.2, 139.8, 148.2 (d), 148.5 (d), 151.9 (d), 152.2 (d), 153.6, 153.8, 156.2. Elem. Anal. Calcd. for C\(_{23}\)H\(_{16}\)F\(_2\): C, 83.62; H, 4.88. Found: C, 82.66; H, 5.22.

Fabrication of EL Devices

The light-emitting devices were prepared on ITO-coated glass substrates, which were pre-cleaned and treated with UV ozone for 3 min before use. The poly(ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) was purchased from Bayer Co. The PEDOT layer was spin-coated with a spin rate of 6500 rpm onto the pretreated ITO substrates and cured at 200°C for 10 min under vacuum. The emissive layer was then spin-coated on the top of the hole-transporting layer from a toluene solution of the polymer (0.6% in wt/v) with a spin rate of 1200 rpm. The thickness of the organic layer was measured on a Sloan Dektak 3030 surface profiler. The PEDOT layer was about 40–50 nm, and the thickness of the polymer layer was about 80–100 nm. A layer of 35-nm thick calcium (Ca) cathode was vacuum-deposited at a pressure of about \(8 \times 10^{-7}\) Torr. An additional protecting layer of 100-nm thick aluminum (Al) was then vacuum-evaporated on top of the Ca layer under the same condition.

RESULTS AND DISCUSSION

Polymer Synthesis

Table 1 summarizes the conditions and results of the polymerization of the fluorene-substituted acetylenic monomers, using WCl\(_6\), MoCl\(_5\), and TaCl\(_5\) as catalysts, and \(n\)-Bu\(_4\)Sn as a cocatalyst. The polymerization reactions were carried out in toluene at either 30 or 80°C. Monomer M1 belongs to a mono-substituted acetylene. Both mixtures of WCl\(_6\)/\(n\)-Bu\(_4\)Sn and MoCl\(_5\)/\(n\)-Bu\(_4\)Sn are known to be active catalysts for the metathesis polymerization of mono-substituted acetylenes. In our study, the polymerization results of both catalyst mixtures are slightly different. A higher yield and number-average molecular weight were achieved for PFA1 by using the WCl\(_6\)/\(n\)-Bu\(_4\)Sn as catalysts. The results demonstrate that M1 can be polymerized even though it contains a bulky fluorene side group. Our results were agreed with many previous reports, which showed that the mono-substituted acetylenes can be polymerized without steric effect.

Monomers M2–M5 belong to disubstituted acetylenes. According to the reports, the TaCl\(_5\)/\(n\)-Bu\(_4\)Sn mixture is known to be an active catalyst for the polymerization of sterically hindered diarylacetylene derivatives. Both monomers M2 and M3, which contain an alkyl and a fluorenyl substituents, were polymerized by TaCl\(_5\)/\(n\)-Bu\(_4\)Sn in toluene at 80°C for 24 h, yielding PFA2 and PFA3 with \(M_n\) of \(~8\) KDa in \(~30\)% yield. Besides, M4 and M5, which contain a phenyl and...
a fluorenyl substituents, were polymerized by TaCl5/n-Bu4Sn in the same conditions, giving PFA4 and PFA5 with $M_n$ of $\sim$300 KDa in satisfactory yields ($\sim$70%). Comparing the polymerization results for PFA2–PFA5, we observed that the alkyl side group would hinder the metathesis polymerization of disubstituted acetylenes to produce PFA2 and PFA3 with lower molecular weights and yields.

Structure Characterization

Figure 1(b,d) shows the IR spectra of polymers PFA1 and PFA2, respectively; for comparison, the spectra of their corresponding monomers M1 and M2 [Fig. 1(a,c)] are also given. The monomer M1 absorbs at 2130, 3293, and 630 cm$^{-1}$, due to the $\equiv$C$-$ stretching, $\equiv$C$-$H stretching, and bending vibrations, respectively. All these acetylene absorption bands disappear in the spectrum of PFA1, but the double-bond $\equiv$C$-$H stretching at 3010 cm$^{-1}$ appears, indicating that the acetylene triple bonds have been transformed to the polyene double bonds by the polymerization reaction. The monomer M2 absorbs at 2226 and 2185 cm$^{-1}$, due to the C=C stretching, which disappear in the spectrum of PFA2. Instead, the double bond C=C stretching at 1650 cm$^{-1}$ appears. It has been reported by Simonescu and Percec that the cis- and trans-PPA can be determined by the $\equiv$C$-$H out of plane and in plane deformation vibrations. The bands at 740, 895, and 1380 cm$^{-1}$ are specific for cis-PPA, and the bands at 922, 970, and 1265 cm$^{-1}$ are specific for trans-PPA. Comparing the spectra of M1 and PFA1, most of the absorption bands in the figure-print region are very similar. Therefore, it is difficult to identify the cis- and trans- contents of PFA1 by IR spectra.

The NMR analysis offers more detailed information on the molecular structure of the polymers. As shown in Figure 2(b), in the $^1$H NMR spectrum of PFA1, there are no peaks in the absorption region of the acetylene protons ($\delta \sim 3.1$ ppm). Instead, a broad peak appears in the olefin and aromatic protons absorption region ($\delta \sim 6.8–8.0$ ppm). It has been reported by Simonescu and Percec that trans-olefin proton peak appears at 6.85 ppm and cis-olefin proton peak appears at 5.82 ppm. We can conclude that PFA1
synthesized by WCl₆ catalyst is a 100% trans structure. Since PFA₂–PFA₅ belong to disubstituted polyacetylenes, they contain no olefinic protons. Therefore, it is impossible to identify their geometric isomers by ¹H NMR spectra.

The thermal properties of fluorene-containing polyacetylenes (PFAs) were investigated by TGA and DSC and summarized in Table 1. Figure 3 depicts the TGA traces of the polymers. PFAs show good thermal stability and their thermal degradation temperatures ($T_d$) at 5% weight loss range from 370 to 503 °C. PFA₁ shows the lowest $T_d$ at 371 °C and PFA₅ reveals the highest $T_d$ at 503 °C. The glass-transition temperatures ($T_g$) are in the range from 76 to 84 °C. Again, the diaryl-substituted PFA₄ and PFA₅ exhibit higher $T_g$ values. Furthermore, the polymers are soluble in common organic solvents, such as THF, chloroform, toluene, and xylene.

### Optical Properties

Figure 4(a,b) depict the UV–vis absorption spectra of PFA₁–PFA₅ in chloroform and in thin film state. For each polymer, both absorption spectra in the solution and in thin film state are very similar except for some peaks, which show a little redshift in the thin film state. This is reasonable since more chain aggregation occurs in the solid state. Comparing the five spectra of PFA₁–PFA₅ in the thin film state, all polymers display an absorption peak near 310 nm, which is associated with the absorption peak of the fluorenyl side groups²⁶ and one or two broad absorption bands in the 350–550 nm region, which is attributed to the $\pi-\pi^*$ interband transition of the main chains.³⁴

Figure 5(a,b) exhibit the PL spectra of PFA₁–PFA₅ in chloroform and in thin film state. PFA₁ with a monofluorenyl substituent shows a maxi-
mum emission at 402 nm in chloroform. Its PL quantum efficiency ($\psi_f$) in chloroform is only 0.08. Theoretically, low luminescent efficiency is the result of solitons generation of the trans-structure of PFA1. Soliton formation is experimentally verified in an iodine-doped PFA1, causing to a new peak in the absorption spectrum. The result agrees with the PPA reported by Sun et al.\textsuperscript{11}

PFA2 and PFA3 belong to alkyl- and fluorenyl-substituted polyacetylenes, and emit a blue-green light at 483 nm in chloroform. Both $\psi_f$ values of PFA2 and PFA3 are 0.79 and 0.85. PFA4 and PFA5 contain the phenyl- and fluorenyl-substituents in the polyacetylene main chains, and emit a green to yellowish green light at 541 and 552 nm in chloroform. Both $\psi_f$ values are 0.50 and 0.42, respectively. These values are smaller than those of PFA2 and PFA3. This could be due to more interchain quenching in the PFA4 and PFA5 system. Table 2 summarizes the UV–vis absorption and PL properties of PFA1–PFA5.

### Electrochemical Properties

Cyclic voltammetry (CV) was employed to evaluate the ionization potential (i.e. hole-injection ability) and the redox stability of our PFAs. The oxidation and reduction potentials were used to determine the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbital energy levels, which were calculated using the internal standard value of $-4.4$ eV with respect to the vacuum level. The anodic sweeps of PFAs (Fig. 6) were reversible and the oxidation onsets occurred at potentials of $+0.64$ to $+0.72$ V for PFA1–PFA5. These oxidation potentials give HOMO energy levels ranging from $-5.04$ to $-5.26$ eV for PFA1–PFA5. The cathodic wave was not observed in acetonitrile solution for all of the polymers within solvent limit. However, the energy band gaps of PFAs can be estimated by the absorption onsets of their UV spectra. Using this approach, the calculated band gaps of PFA1–PFA5 are in the range from 2.32 to 2.95 eV. The LUMO energy levels of PFA1–PFA5 can be also estimated from optical band gaps and HOMO energy levels. The HOMO and LUMO energies levels of PFA1–PFA5 are listed in Table 2, and the band diagrams of PFAs are shown in Figure 7. In this paper, the effects of substituents on the energy band gaps of the substituted polyacetylenes are investigated. Basically, there are two substitution related effects, electronic effect, and steric hindrance. Comparing the energy band gap of PFA1 with those of the other disubstituted polyacetylenes, PFA1s shows a much smaller energy band gap. This is because PFA1 has less steric effect and has longer conjugation length for the polyene main chains. In PFA2 and PFA4 case, PFA2 contains alkyl and fluorenyl substituents, while PFA4 contains phenyl and fluorenyl substituents. PFA2 shows a much larger energy band gap than PFA4. This is because the alkyl substituent has larger steric effect than the phenyl substituent. In the case of PFA4 and PFA5, the difference between two polymers is on the difluoro substituents. PFA5 with a 2,3-difluorophenyl substituent exhibits a smaller energy

<table>
<thead>
<tr>
<th>Table 2. Optical Properties, Quantum Yields, and Redox Properties of PFA Polymers</th>
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<tbody>
<tr>
<td>Polymer</td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>PFA1</td>
</tr>
<tr>
<td>PFA2</td>
</tr>
<tr>
<td>PFA3</td>
</tr>
<tr>
<td>PFA4</td>
</tr>
<tr>
<td>PFA5</td>
</tr>
<tr>
<td>a Measured in chloroform.</td>
</tr>
<tr>
<td>b Prepared by spin-coating from toluene solution.</td>
</tr>
<tr>
<td>c Data in the parentheses are wavelength of shoulders.</td>
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<tr>
<td>d Excited at $\lambda_{max}$ of abs.</td>
</tr>
<tr>
<td>e Measured by integral sphere in chloroform.</td>
</tr>
<tr>
<td>f The optical band gap takes as the absorption onset of UV–vis spectrum of the polymer film.</td>
</tr>
<tr>
<td>g HOMO/LUMO values as determined by the onset of CV measurements and optical band gap.</td>
</tr>
</tbody>
</table>
band gap. This is due to the less electron withdrawing effect for the 2,3-difluorophenyl substituent than that of a phenyl substituent. The results are consistent with those reported by Sun et al. 14

EL Properties and LED Devices

To evaluate the potential application of PFAs in PLED, we fabricated a double-layered device with the configuration of ITO/PEDOT/PFAs/Ca/Al. The EL spectra (Fig. 8) of the PFAs are similar to their corresponding PL spectra (Fig. 4). This indicates that both the PL and EL spectra originate from the same radiative decay process of single excitons. Both PFAs2 and PFAs3 emit a blue light with peaks at 472 and 468 nm, respectively, while PFAs4 and PFAs5 emit an orange-red light with peaks at 576 and 602 nm, respectively. Besides, we don’t observe the aggregate emission at a long wavelength, compared with the PL and EL spectra of polyfluorenes.23 This means that the PFAs are more stable emitting materials than polyfluorenes.

Figure 9 exhibits the current density-luminance-voltage (I-L-V) plots for the devices fabricated with an emitting layer of PFAs2 and PFAs3. The turn-on voltage of a PFAs2 device is 6 V, with a maximum brightness of 100 cd/m² at 14.5 V, whereas the turn-on voltage of a PFAs3 device is 6.3 V, with a maximum brightness of 77 cd/m² at 15 V. Both devices have much better performance.
than the blue devices based on poly(1-alkyl-2-phenylacetylene) reported in the literature. This is because introducing the fluorene groups into the polyacetylene backbones would improve the charge injection of polymers, since PFAs show higher HOMO energy levels than poly(1-alkyl-2-phenylacetylene).

Figure 10 depicts the I-L-V characteristics of the PLED devices fabricated with PFA4 and PFA5. The turn-on voltage of a PFA4 device is 4.5 V, with a maximum brightness of 111 cd/m² at 8.5 V, while the turn-on voltage of a PFA5 device is 2.8 V, with a maximum brightness of 923 cd/m² at 8 V. The PFA5 device performance is the best for the red light devices based on polyacetylenes so far reported in the literatures.

Furthermore, it has been proven that a white PLED can be achieved by blending a blue host polymer and an orange-red guest polymer. We used PFA2 as a host material, which was blended with 2 wt % of PFA5 to yield a white light device. Figure 11 shows the EL spectra of the blended device. The EL intensity is increased as the voltage increases. However, no obvious color change is observed when the voltage increases. The CIE device coordinates ranges (0.33, 0.39) from 6 to 10 V. This demonstrates that PFAs are thermally stable when they are used as emitting layers in PLED. The I-L-V characteristics of blended polymers are shown in Figure 12. The turn-on voltage of this device is 6.0 V with a maximum current efficiency of 1.4 cd/A and a maximum brightness of 450 cd/m² at 15 V. This is a first highly efficient white light PLED device.

![Figure 9](image9.png)

**Figure 9.** Current density and luminescence intensity-voltage characteristics for PFA2 and PFA3 in ITO/PEDOT/Polymer PFA2 or PFA3/Ca/Al device.

![Figure 10](image10.png)

**Figure 10.** Current density and luminescence intensity-voltage characteristics for PFA4 and PFA5 in ITO/PEDOT/Polymer PFA4 or PFA5/Ca/Al device.

![Figure 11](image11.png)

**Figure 11.** EL spectra measured at different voltage for the device: ITO/PEDOT/PFA2 (98 wt %) + PFA5 (2 wt %)/Ca/Al device.

![Figure 12](image12.png)

**Figure 12.** Luminescence and yield-voltage characteristics for the white light device: ITO/PEDOT/PFA2 (98%) + PFA5 (2%)/Ca/Al device.
based on polyacetylenes. Table 3 summarizes the performances of the EL devices for the PFAs.

### CONCLUSIONS

Five novel polyacetylenes containing fluorene side groups were successfully synthesized and characterized. The fluorene-substituted acetylene monomers can be polymerized by using WCl$_6$/n-Bu$_4$Sn, MoCl$_5$/n-Bu$_4$Sn, and TaCl$_5$/n-Bu$_4$Sn as catalysts. Most of the PFAs were obtained in high molecular weights and reasonable yields. The monofluorenyl-substituted polyacetylene PFA1 shows a maximum emission at 402 nm. Its PL efficiency in chloroform is only 0.08. Its EL property is too weak to be measured. However, PFA2–PFA5 belong to disubstituted polyacetylenes. The bulky alkyl, phenyl, and fluorenyl groups were introduced to increase the steric hindrance and prevent close packing of the main chains. Both PFA2 and PFA3 emit blue-green light at 483 nm, while PFA4 and PFA5 emit a green to yellowish-green light at 541 and 552 nm in solution, respectively.

According to the CV results, the HOMO energy levels of PFA2–PFA5 are located from 5.04 to 5.24 eV, which are higher than those of the disubstituted polyacetylenes reported in the literatures. It means that the hole injection from ITO anode is much easier. This is the reason why PFA2–PFA5 show much higher EL efficiency than the other disubstituted polyacetylenes. A device fabricated by PFA5, with the configuration of ITO/PEDOT:PSS/PFA5/Ca/Al, revealed a turn-on voltage at 2.8 V and a maximum brightness of 923 cd/m$^2$ at 8 V. This is the highest value for polyacetylenes reported in the literature so far. Furthermore, a white light PLED device based on the blending of 98 wt % of PFA2 and 2 wt % PFA5 was also fabricated. The device shows a maximum current efficiency of 1.3 cd/A at 6 V and a maximum luminance of 450 cd/m$^2$ at 15 V. All these results demonstrate that disubstituted polyacetylenes are potential candidates for PLED applications.

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### REFERENCES AND NOTES


<table>
<thead>
<tr>
<th>Polymer</th>
<th>EL Emission $\lambda_{max}$ (nm)$^a$</th>
<th>CIE Coordinate (x,y)$^a$</th>
<th>Turn-on Voltage (V)$^b$</th>
<th>Max Current Efficiency (cd/A)</th>
<th>Max Brightness cd/m$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFA2</td>
<td>472</td>
<td>(0.18,0.24)</td>
<td>6.0</td>
<td>0.03</td>
<td>100</td>
</tr>
<tr>
<td>PFA3</td>
<td>468</td>
<td>(0.17,0.18)</td>
<td>6.3</td>
<td>0.06</td>
<td>77</td>
</tr>
<tr>
<td>PFA4</td>
<td>576</td>
<td>(0.49,0.50)</td>
<td>4.5</td>
<td>0.07</td>
<td>111</td>
</tr>
<tr>
<td>PFA5</td>
<td>604</td>
<td>(0.54,0.45)</td>
<td>2.8</td>
<td>0.44</td>
<td>923</td>
</tr>
<tr>
<td>PFA2 (98 wt %) + PFA5 (2 wt %)</td>
<td>460,560</td>
<td>(0.33,0.39)</td>
<td>6.0</td>
<td>1.40</td>
<td>450</td>
</tr>
</tbody>
</table>

$^a$ Recorded at 20 mA/cm$^2$.
$^b$ Recorded at 1 cd/m$^2$.  

Table 3. The EL Device Performances for PFA2–PFA5