Ladder-Type Oligo(*p*-phenylene)s Tethered to a Poly(alkylene) Main Chain: The Orthogonal Approach to Functional Light-Emitting Polymers

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ABSTRACT: We report a series of light-emitting polymers with ladder-type oligo(*p*-phenylene) units orthogonally and periodically tethered to a polyalkylene main chain via a substitution-type condensation polymerization reaction. This involved the reaction between lithiated fluoreneacene oligomers and a homologous series of α,ω-dibromoalkanes. The fluoreneacene oligomers were synthesized using a step-by-step procedure involving the Suzuki coupling method, Grignard reaction, and Friedel–Crafts type ring closure (alkylation). The polymerization involved lithiation of the reactive hydrogens in the middle phenyl group followed by an S_N2-type condensation polymerization with the dibromoalkanes. The oligomers have spectral properties consistent with that of other ladder-type *p*-pheneneylene structures. The alkylene chain length influenced the luminophore aggregation and excimer formation in the solid state. These materials showed high photoluminescence efficiencies in both solution and solid state, making them good candidates as organic materials for light-emitting devices.

Introduction

A "ladder polymer" is defined as an uninterrupted series of rings connected by sterically restrictive links around which rotation cannot occur without bond rupture.[1] For its synthesis, two approaches can be generalized.[2] The first approach employs polymerization of multifunctional monomers, in which both strands of the ladder structure are generated at the same time. The second approach involves the cyclization of suitably functionalized single-stranded or open-chain precursor polymers via polymer analogous reactions.

In 1991, the first synthesis of a soluble, fully conjugated ladder-type polymer, a poly(*p*-phenylene)-type ribbon or ladder-PPP (LPPP), marked an important step in polyarylene chemistry (Figure 1).[3] In general, the synthetic procedure involved (1) the generation of a suitably functionalized, single-stranded poly(*p*-phenylene) (PPP) precursor and (2) a polymer-analogous cyclization, e.g., Friedel–Crafts-type alkylation reaction. It was possible to design efficient multicolor (blue-green, yellow, and red), polymer-based light-emitting diode (LED) devices based on LPPP-type materials.[4] These LEDs showed high electroluminescence (EL) with quantum efficiencies up to 4% (applied voltages: 4–9 V). LPPPs have also been applied in optically pumped, blue solid-state lasers in open cavity and distributed feedback (DFB) configuration.[5] They are characterized by large charge carrier mobilities (up to 10^{-3} cm²/(V s) for holes at room temperature) and longer conjugation persistence length. The unique performance of these polymers is related to an extraordinary low concentration of electronically active traps. Thus, this set of attractive properties has established LPPP as widely useful materials for organic polymer-based optical and electrooptical applications.[2,6,7]

Along with LPPPs, polyfluorenes are an important class of electroluminescent polymer materials (Figure 1). It emits blue light showing high quantum yields and
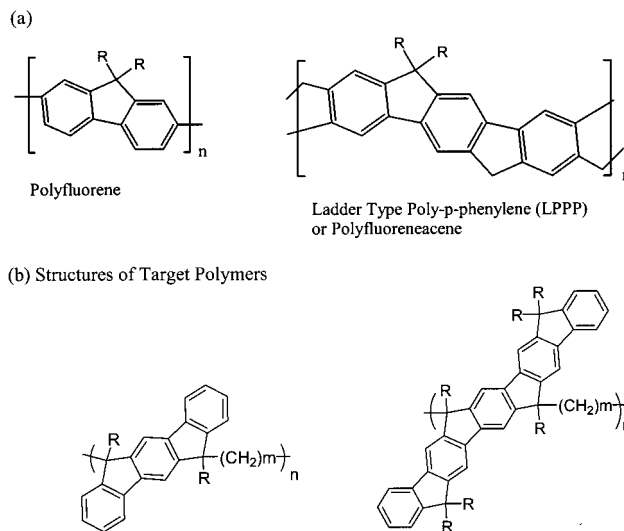
(a)

(b) Structures of Target Polymers

Figure 1. Chemical structure of (a) polyfluorenes, ladder-type poly(*p*-pheneylene)s (LPPP)s, and (b) target poly(alkylenefluoreneacence) polymers.

has been extensively studied during the past few years.[8] One of the problems is the excimer formation through chain aggregation that tends to lower electroluminescence efficiency. This is prevalent with most conjugated polymers primarily due to the nature of π-stacking among aromatic rings. To overcome this drawback, cross-linkable polyfluorene with a styrene group has been made recently by Miller et al.[9] The immobilization of the polymer chain by cross-linking diminished the aggregation of the polymer chains.

In a recent paper, Galvin et al. reported the synthesis of novel polymer structures where the ladder-type tri-(*p*-phenylene) is oriented orthogonal and periodically with respect to the poly(phenylenevinylene) (OPV) backbone.[10] Such an orthogonal structure was expected to decrease the quenching processes of excitons by preventing the aggregation of the OPV units, thus increasing the electroluminescence quantum efficiency

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and device stability. Since the conjugation length of the OPV segment is defined and adjustable, the color of the emission was expected to be easily controlled.

Another approach to electroluminescent materials is to use polymers with discrete luminophore units. This type of electroluminescent polymer contains a nonconjugated polymer backbone with pendant luminophore or a main chain with the conjugated moieties separated by the nonconjugated part.[11,12,20] It has been shown that a variety of these polymers are highly luminescent in both solution and solid state.[13] Since the luminophores are isolated, the conjugation of the π-system is confined, and the color of the emission can be tailored.[11] The investigation of functional oligomers of this type has recently gained much attention due to their analogous properties with monodispersed polymer systems and interesting electrooptical properties.[14] They serve as important model systems for understanding electrooptical phenomena in conjugated polymers.

In this paper, we report a new method where conjugated fluoreneacene (oligomers of LPPP) luminophore units are tethered in a periodic orthogonal position with respect to a polymer backbone and separated by discrete nonconjugated alkylene chains (Figure 1).[15] The oligofluoreneacene luminophores consist of alternating five- and six-membered all-carbon rings having a defined conjugation length. These conjugated units can be tuned to control the emission color and efficiency of emitting materials.[16] We have chosen to synthesize these luminophores using a step-by-step synthesis scheme to obtain monodispersed target oligomers having two reactive hydrogens for lithiation. The polymers were synthesized by reacting with α,ω-dibromoalkanes via a condensation type of polymerization in solution.[18] To our knowledge, this is the first reported polymerization of lithiated oligomeric fluoreneacenes with dibromoalkanes via an S_N2 type of mechanism. The structure and properties of the oligomers and polymers were characterized and compared to previously reported analogous materials. The physical and spectral properties of these materials are discussed with respect to the alkylene spacer chain length.

Results and Discussion

Fluoreneacene Oligomer Synthesis. The synthetic route for the fluoreneacence oligomers and the polymers are shown in Scheme 1. The Pd(0)-catalyzed Suzuki coupling[17] gave high yields in preparing the tri- and pentafluoreneacene compounds. This was followed by a Grignard reaction to convert the aldehyde to an alcohol and a Friedel–Crafts ring closure (alkylation) reaction. The step-by-step synthesis of the septamer is currently in progress.[2] It should be noted that most of the previous work on LPPP oligomers involved stoichiometric coupling reactions which resulted in mixed products separable only by chromatographic methods.[2,16] In our case a rational step-by-step synthesis resulted in monodispersed oligomers.[10] The yields of this reaction were normally higher than 80%. It is also worth noting that a bulky phenyl group was necessary to avoid the intermolecular coupling side reaction and confer regioselectivity in the ring closure step.[2,16] Our initial effort with an *n*-alkyl derivative (via Grignard reaction) followed by ring closure with $BF_3 \cdot Et_2O$ resulted in cross-linked products. Applying a bulky group (phenyl or *tert*-butyl group) can eliminate the intermolecular Friedel–Crafts reaction and the possibility of β-elimination.[16]

Figure 2 shows the COSY spectrum of fluoreneacene pentamer **m-5**. The correlation between the aliphatic and aromatic proton peaks can be clearly interpreted from the spectrum. The chemical shift of the protons from the ninth position of the middle phenyl ring in the fluoreneacene oligomer shifts to a lower field (at 5.17 ppm) for **m-5** compared with **m-3**, which is located at 5.07 ppm. The presence of this peak is significant for confirming oligomer reactivity for lithiation. Figure 3 shows a computer-generated three-dimensional structure of the oligomer **m-5** using MM2 calculations and MOPAC for energy minimization (Chem 3-D software). Some torsion between the adjacent rings occurs but is considerably less than 28° for oligo(*p*-phenylene)s.[20] Because of the ladder structures, better conjugation can be expected between the phenyl rings on an oligophenylene structure with a similar length.

Polymerization with α,ω-Dibromoalkanes. Our group recently reported the polymerization of α,ω-dibromoalkanes and a lithium-activated fluorene at the ninth position to form poly(fluoren-9,9-diyl-*alt*-alkan-α,ω-diyl) or polyalkylenefluorene polymers via an S_N2 substitution mechanism.[18] Like fluorene, the oligofluoreneacene ring system has a reactive remaining proton at the ninth position that can be activated by a strong base such as *n*-butyllithium or sodium hydride. After forming the lithium complex, it readily reacted with the α,ω-dibromoalkane to form polymeric materials. The polymerization was allowed to proceed at room temperature after activation by butyllithium at 0 °C.[18] Amorphous soluble polymers were obtained through this polymerization process. The molecular weight of the polymers was characterized by SEC in THF using polystyrene as the standard. The characteristics of the polymers are summarized in Table 1. Similar to the poly(malonic ester) condensation polymerizations involving the nucleophilic attack on α,ω-dibromoalkanes, the molecular weights of these polymers are low with a high polydispersity.[18c] For the poly(malonic ester)s, the mechanism involves a propagation reaction competing with ring cyclization of the alkylene units,[18d] giving molecular weights of the order of 800−20 000 g/mol.[18e] However, several differences can be noted: (a) in this system, the anions are separated in a *p*-dibenzylic position, (b) the tendency for cyclization of the α,ω-dibromoalkanes is avoided, and (c) the presence of a bulky phenyl group can hinder the propagation step. Nevertheless, the obtained molecular weights are very useful for investigating spectral behavior with luminophore separation via alkylene spacer units (see spectral properties), a major objective of this work.

As with the reaction of anions, lowering the reaction temperature resulted in a narrower polydispersity. The polymerization mechanism is also believed to proceed via an S_N2 substitution mechanism. The longer α,ω-dibromoalkanes resulted in relatively higher molecular weights. With the incorporation of longer alkylene units in the main chain, the glass transition temperature (T_g) was observed to decrease. The results are summarized in Table 1. The difference in temperature was as much as 35 °C between **P-3-8** and **P-3-4**. No liquid crystalline behavior was detected for the **P-3-n** polymers by DSC. We also observed that the reactivity of the lithiated oligomers decreased with increasing size of the oligofluoreneacene; i.e., the trimer **m-3** is more reactive than pentamer **m-5**. Our attempts to polymerize the pentamer **m-5** repeatedly were not successful using the

Synthesis of m-3 and polymers

m=8 **p-3-8**
m=6 **p-3-6**
m=5 **p-3-5**
m=4 **p-3-4**
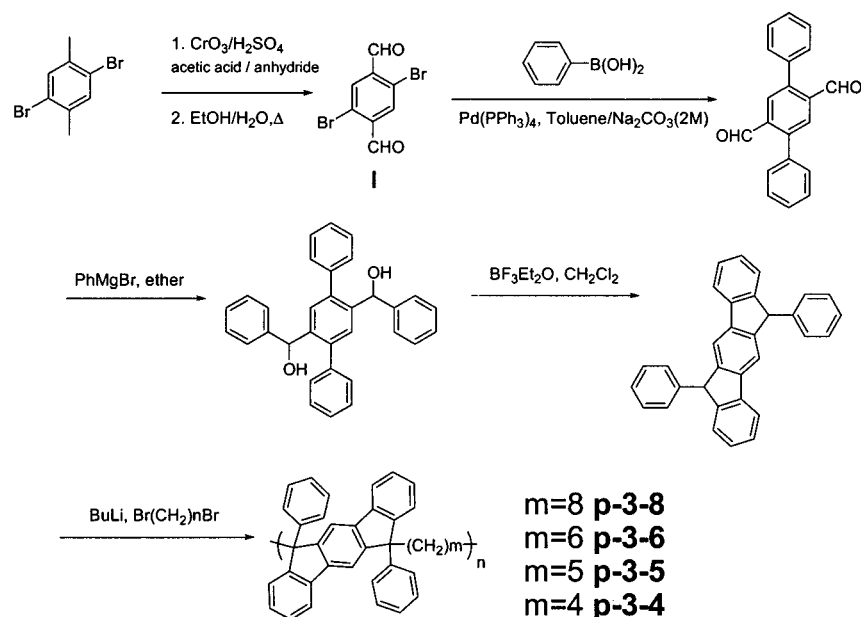
synthesis of m-5 and attempted polymerization
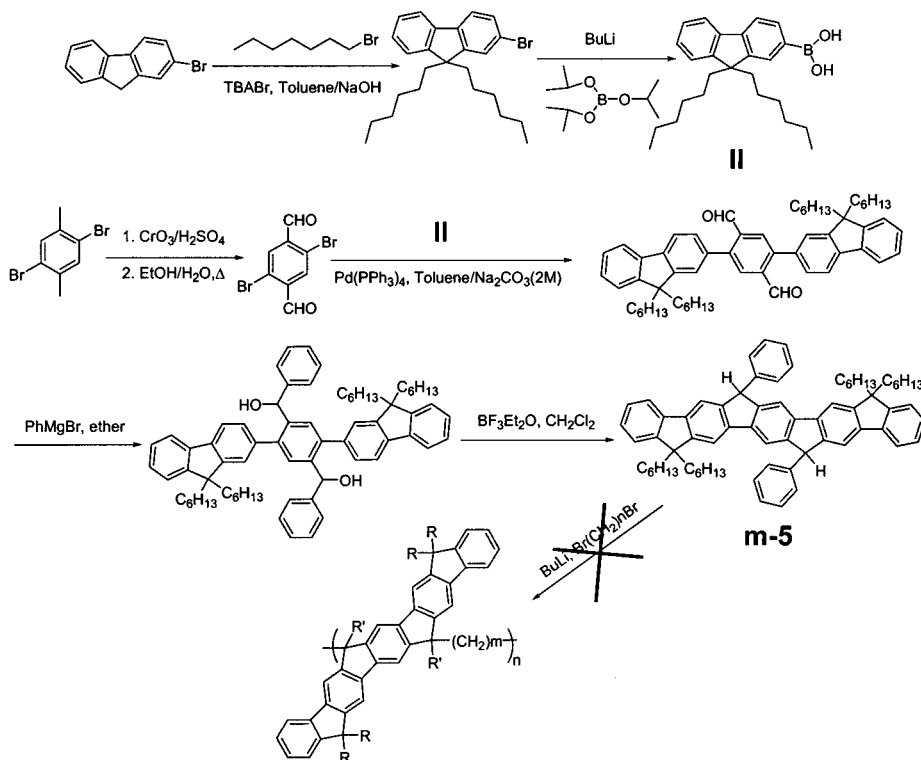
present polymerization method and conditions. This could be due to lack of reactivity of the lithium complex, solubility differences, and steric hindrance of the phenyl group. Further investigations are currently being done to understand polymerizability with model compounds and with different reaction conditions.

Figure 4 shows the NMR spectrum of the polymer **P-3-8**. From the spectrum, the broadening of the peaks indicates the formation of a polymeric structure. The position of the peaks also correlated with a linear structure for the polymer, indicating the absence of any cross-linking. The peaks in the lower field region are attributed to the aromatic protons of the fluoreneacene trimer, and the proton at 2.62 ppm was due to the methylene units at the α-position to the phenyl ring system. The rest of the alkylene protons are observed
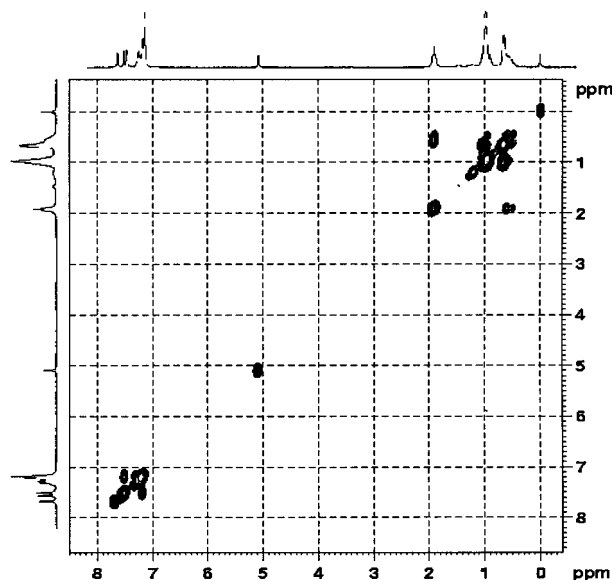
Figure 2. Two-dimensional COSY spectrum of **m-5** pentamer showing the correlation for the aromatic and aliphatic proton peaks. They are downfield compared to the **m-3** trimer, suggesting the effect of a higher conjugation length with the pentamer.
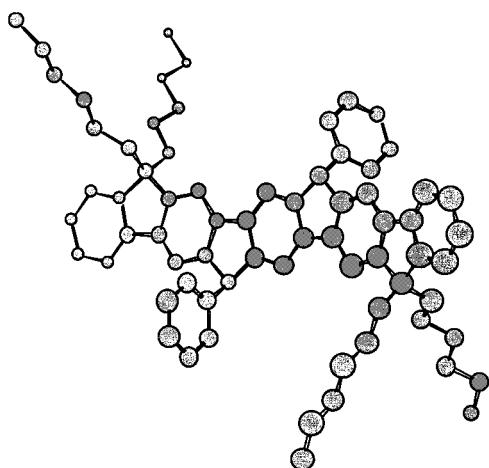

Figure 3. Computer-generated 3-D structure of **m-5** illustrating the significant planarity on the phenyl rings resulting from the ladder structure.

Table 1. Characteristics of the Polymers

	M_n	PDI	T_g (°C)	elemental analysis
P-3-8	3470	2.06	119	C, 91.19; H, 7.02
P-3-6	3240	2.50	123	C, 91.42; H, 6.37
P-3-5	2780	2.42	152	C, 92.05; H, 6.43
P-3-4	2950	2.52	154	C, 92.35; H, 6.41

at higher field. Also notable is the absence of the proton shift at 5.07 ppm, which is attributed to the ninth position of the middle phenyl ring in an unreacted fluoreneacene oligomer. The ^{13}C NMR was also consistent with the polymer structure.

Spectroscopic Properties and Aggregation. Conjugated polymers like LPPP are expected to have extensive π-stacking behavior and aggregation, which is unfavorable to excimer formation.[8] Conjugated oligomers are also aggregated due to strong π-stacking behavior and have higher crystallinity.[14] The present polymer structure allows the investigation on the extent of excimer formation between the luminophore units separated by alkylene spacer units. Earlier studies have
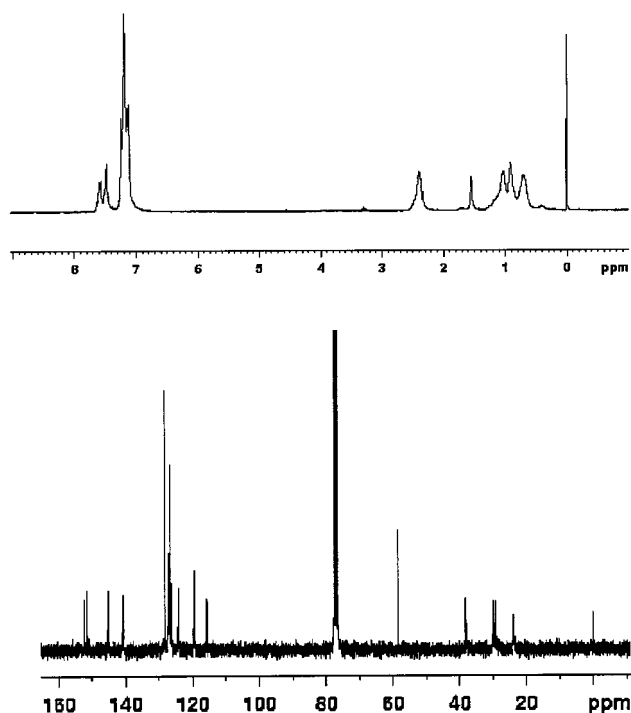

Figure 4. NMR spectra of **P-3-8** polymer showing peak broadening with polymerization. The ^{13}C NMR assignments are consistent with the structure and are further outlined in the experimental part.
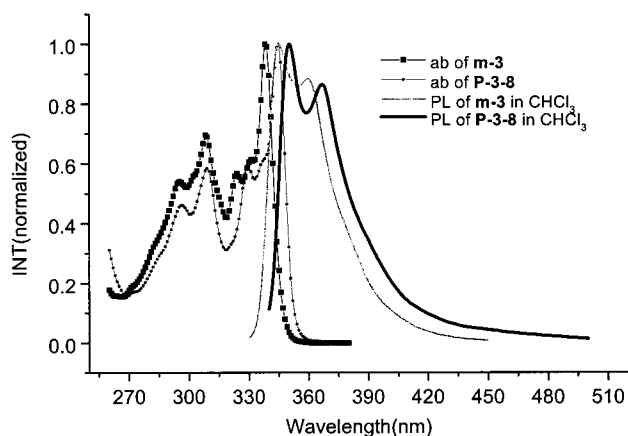

Figure 5. Spectroscopic properties of **m-3** and **P-3-8** in solution showing the absorbance and photoluminescence behavior.

shown that molecules consisting of luminophores separated by C–C single bonds of alkyl chains may exhibit unusual luminescence properties due to the intramolecular excimer formation.[19] This excimer formation usually results in a longer wavelength and featureless emission that depends on the distance between the luminophores.

Figure 5 shows the absorption and emission spectra of the oligofluoreneacene trimer and corresponding **P-3-8** polymer in chloroform solution. The absorption maxima of **m-3** and **P-3-8** in solution are at 338 and 345 nm, respectively. A small red shift for the polymer was observed. The photoluminescence in solution also showed this shift. All the photoluminescence of the **P-3-n** polymers showed identical shape in chloroform solution regardless of the alkylene spacer chain length. The results are summarized in Table 2. However, the PL of the films shown in Figure 6 is different from that
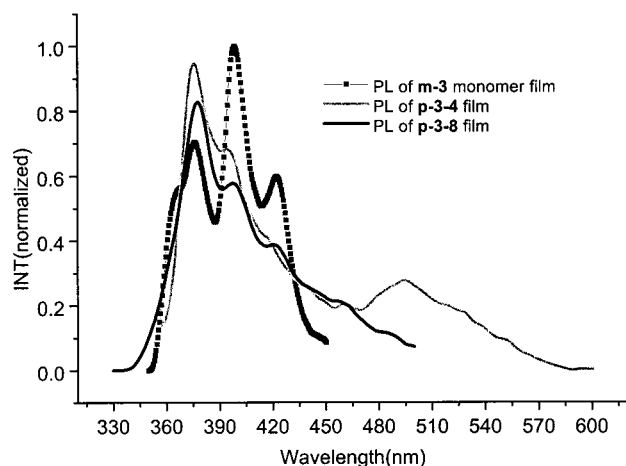
Figure 6. PL of the film of **m-3**, **P-3-4,** and **P-3-8** showing the fine structure and the presence of aggregations (excimer) for **P-3-4** polymer.

Table 2. Optical Properties of the Monomers and the Polymers

	absorption in CHCl$_3$ (nm)	PL in CHCl$_3$ (nm)	PL of film (nm)	quantum yield (φ)
m-3	328	345, 360	376, 399, 423	0.36
P-3-8	345	350, 367	377, 398	0.58
P-3-6	340	346, 361	377, 397	0.51
P-3-5	342	348, 365	376, 398	0.45
P-3-4	344	350, 366	375, 395, 495	0.44
m-5	390	395, 419	434, 461	0.57

of the solution in both peak position and shape of the spectrum. The monomer film showed three peaks at 376, 399, and 423 nm when excited at 310 nm with the peak at 399 nm having the highest intensity. On the other hand, all polymers have their major peak centered around 376 nm, and only a shoulder is observed at 399 nm. It is worth noting that a longer wavelength emission at 495 nm is observed for **P-3-4** with the shortest alkylene spacer. This emission was not observed for all other polymers films.

Kallitis et al.[20] reported a series of polyethers with laterally attached oligophenyl units in the polymer backbone. In their report, the tri- and pentaphenyl polymers had almost the same emission wavelength, ca. 400 nm. A larger difference should be expected in solution consistent for the longer conjugation length of the pentamer. It is possible that their results were affected by the presence of intramolecular excimer formation due to aggregation or the limited increase in conjugation for the pentamer due to twisting of the phenyl rings. In principle, the oligofluoreneacene ladder structures should show better conjugation and longer wavelength emissions. In our case, a sharper absorption band was observed for the **m-3** trimer compared to the triphenyl reported in the literature.[20] The PL behaviors of **m-3** and **P-3-n** solutions are similar while the **m-5** showed a longer emission wavelength by 57 nm compared to that of the pentaphenyl reported in the literature.[20] Thus, the planarization of the phenyl rings was evident with the longer emission wavelength of the **m-5** pentamer. No chain-length-dependent excimer formation was observed for the **P-3-n** polymers in solution since all polymers had similar spectra. For the film, the featureless emission observed at 495 nm for **P-3-4** can only be attributed to aggregation at the solid state. None was observed for polymers with longer alkylene chain spacers. This phenomenon indicates that
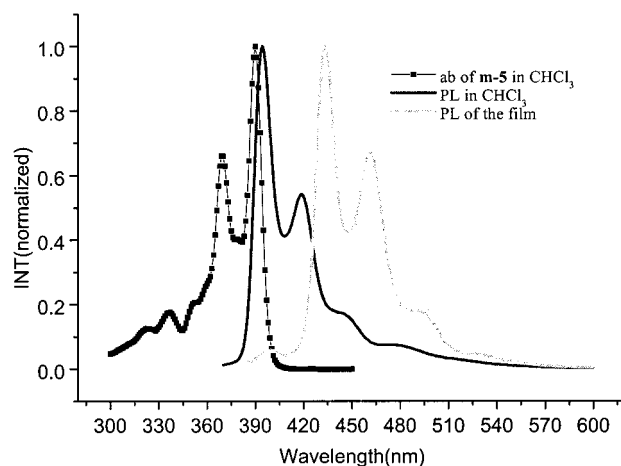

Figure 7. Spectral properties of **m-5** showing the absorbance and PL behavior. A significant red shift is observed on the PL between the solution and film spectra.

for these polymers excimer formation is related to the distance between each orthogonal luminophore in the main chain; i.e., the shorter the alkyl spacer, the stronger the tendency to aggregate intramolecularly, resulting in excimer formation.

Figure 7 shows the spectroscopic properties of the pentamer. As mentioned before, this compound did not readily polymerize via the lithium-activated polymerization. Since this compound showed better quantum efficiency by itself and can be an important blue-light-emitting material, the physical and optical properties as an oligomer were investigated. The absorption of the pentamer is at 390 nm with an onset at 400 nm corresponding to a band gap of 3.1 eV. This absorption is 48 nm shorter than the ladder-type polymer previously made by the Mullen group, which has much higher molecular weight.[3] This observation confirms the strong dependence of absorption on conjugation length for ladder polymer structures. The PL in chloroform solution and film state is at 395 and 434 nm, respectively. The small Stokes shift of the PL from the solution is a result of the rigid geometry of the planar ladder structure. Surprisingly, the PL of the film has a big red shift compared with that of solution, ca. 40 nm, indicating the importance of packing arrangement in the solid state compared to **m-3**. However, the fine structure of the spectra is the same. Several small peaks at 434, 461, 495, and 530 nm for the film and at 395, 419, 446, and 479 nm for the solution can be observed from the spectra. The shape of this spectrum is consistent with that of block copolymers recently reported by Mullen et al. with short oligofluorene blocks.[21]

The PL efficiency of these materials in solution was measured by a standard method using 2-aminopyridine and quinine bisulfate in 0.1 N sulfuric acid as references.[22] The results are summarized in Table 2. The oligomer **m-3** has an efficiency of 0.36. The value increases for the polymer up to 0.44 after incorporating a C-4 alkylene chain. This trend increases to 0.58 for the octylene polymer. The efficiency enhancement of these compounds could be due to the longer distance between the **m-3** chromophore, which reduces the intramolecular π interactions. These results are consistent with observed PL behavior on the **P-3-n** series where excimer formation is observed only for **P-3-4**, resulting in lower quantum efficiency. The oligomer **m-5** has an efficiency of 0.57. Thus, these values are com-
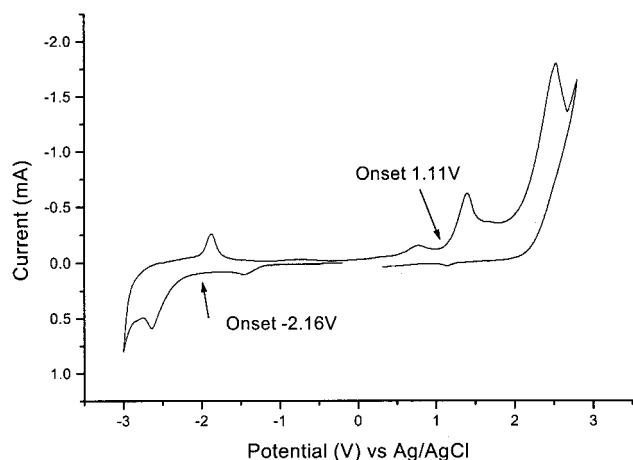
Figure 8. C—V diagram of **m-5** showing the anodic and cathodic peaks for both p-doping and n-doping processes.

parable with other PPP derivatives and lower than those of other ladder-type PPPs of longer conjugation length.[2-7]

Band Gap Behavior of m-5. Cyclic voltammetry was applied to investigate the redox behavior of the pentamer and to estimate the HOMO and LUMO energy levels. The cyclic voltammogram was obtained using monomer-free methylene chloride and tetrabutylammonium hexfluorophosphate (0.1 M) as supporting electrolyte with a scan rate of 20 mV/s. The working electrode was a gold substrate with spin-casted film, and a platinum wire was used as counter electrode. Figure 8 shows the C—V trace of both the n-doping and p-doping processes. The film showed a pseudo-reversible n-doping process and an irreversible p-doping process. The cathodic peak was exhibited at −2.63 V (vs Ag/AgCl) with corresponding anodic peak at −1.88 V(vs Ag/AgCl). The onset potential of the reduction was −2.16 V(vs Ag/AgCl). In the oxidation curve, the anodic peak was at 1.39 V (vs Ag/AgCl) with an onset at 1.11 V(vs Ag/AgCl). From these onset values, the band gap of this material was estimated to be 3.27 eV, a little larger than that estimated from the absorption onset. According to the literature,[23] the onset potentials can be utilized to estimate the HOMO and LUMO energy levels. The calculated HOMO and LUMO energy of this material are 5.5 and 2.2 eV, respectively. These energy levels are similar to values calculated by Bredas for PPP.[24]

Conclusion

A series of polymers with orthogonal oligomeric fluoreneacene units tethered to polyalkylene main chain were synthesized via a lithiation-activated S_N2 condensation polymerization reaction. The two fluoreneacene oligomers have different spectral properties and reactivity consistent with a ladder-type structure. The polymers have low molecular weights and broad polydispersity, typical of S_N2 condensation polymerizations. The spectral properties and redox properties have also been studied and compared with analogous PPP and LPPP polymers. The alkylene chain length influenced the excimer formation in the solid state. The **m-5** pentamer showed interesting spectral and band gap properties. These materials showed high PL efficiencies in both solution and solid state, which makes them good candidate materials for LED devices. Further investigations will be made for longer fluoreneacene oligomers and understanding the polymerization process.

Experimental Section

Materials. *n*-Butyllithium (2.0 M solution in cyclohexane), 1,4-dibromobutane, 1,6-dibromohexane, 1,8-dibromooctane, 2-bromofluorene, 2,4-dibromo-*p*-xylene, phenylboronic acid, boron trifluoride, 1-bromohexane, tetrabutylammonium bromide, lithium perchlorate, and Pd (PPh$_3$)$_4$ were purchased from Aldrich and used without further purification. Tetrahydrofuran, ethyl ether, and toluene were purchased from Fisher and distilled from a sodium/benzophenone still. Methylene chloride was distilled from calcium hydride prior to use.

Measurements. NMR spectra were collected on a Bruker ARX 300 spectrometer with chloroform-*d* and THF-d_8 solvent and TMS as internal standard. UV—vis and fluorescence spectra were obtained on a Perkin-Elmer Lambda 20 spectrometer and Perkin-Elmer LS50B spectrometer, respectively. Size exclusion chromatography (SEC) was conducted on a Waters chromatography using polystyrene as standard. Differential scanning calorimetry (DSC) measurements were done using a Mettler DSC30. Cyclic voltammetry (CV) was performed on an Amel 2049 potentiostat and Power lab system with a three-electrode cell in a solution of methylene chloride using tratrabutylammonium hexfluorophosphate (0.1 M) as supporting electrolyte and a scan rate of 20 mV/s.

Synthesis. 2,5-Dibromobenzene-1,4-dicarbaldehyde (I). This compound was synthesized according to a published procedure with a little modification.[10] 70 mL of sulfuric acid was added dropwise into a suspension containing 20 g of 2,5-dibromo-*p*-xylene, 100 mL of acetic acid, and 200 mL of acetic anhydride at 0 °C. CrO$_3$ was then added to the mixture in portions. The resulting mixture was stirred vigorously at this temperature for another 5 h until the reaction was completed. The greenish slurry was poured into ice water and filtered. The white solid was washed with water and cold methanol. The diacetate was then hydrolyzed by refluxing with a mixture of 100 mL of water, 100 mL of ethyl alcohol, and 10 mL of sulfuric acid for 5 h. After the mixture cooled, the pale yellow product was separated by filtration. The crude product was purified by recrystallization from chloroform. (11.1 g, 50% overall yield). ^{1}H NMR (CDCl$_3$, ppm): δ 10.34 (s, 2H), 8.16 (s, 2H). ^{13}C NMR (CDCl$_3$, ppm): δ 190.2, 137.7, 135.4, 125.9. Anal. Calcd: C, 32.91; H, 1.38. Found: C, 32.63; H, 1.41.

[1,1′;4′,1″]Terphenyl-2′,5′-dicarbaldehyde (II). This compound was synthesized by the well-known Suzuki coupling method.[17] A mixture of 1.97 g of compound **I**, 2.11 g of phenyl boronic acid, 0.39 g of Pd(PPh$_3$)$_4$, 25 mL of toluene, and 5 mL of 2 M Na$_2$CO$_3$ solution was refluxed at 85 °C for 24 h under nitrogen, then poured into water, and extracted with methylene chloride. The organic layer was washed with brine and water and dried over MgSO$_4$. The crude product was first purified by flash column (methylene chloride as eluent) and then recrystallized form chloroform. 1.93 g of product (yield: 82%) was obtained as pale yellow crystals. ^{1}H NMR (CDCl$_3$, ppm): 10.09 (s, 2H), 8.13 (s, 2H), 7.53, 7.44 (m, 10H). ^{13}C NMR (CDCl$_3$, ppm): δ 192.2, 145.0, 137.0, 136.8, 130.6, 130.5, 129.2, 129.1. Anal. Calcd: C, 83.90; H, 4.93. Found: C, 83.81; H, 4.90.

[5′-(Hydroxyphenylmethyl)-[1,1′;4′,1″]terphenyl-2′-yl]-phenylmethanol (III). A solution of compound **II** (0.724 g) in THF was added dropwise to 3 mL of phenylmagnesium bromide (1.0 M solution in THF) at 0 °C. The reaction mixture was warmed to room temperature for 1 h. After cooling to 0 °C, 10 mL of 1 N HCl was added. The solution was poured into water, extracted with ether, and dried over MgSO$_4$. 0.952 g of product (yield: 85%) was obtained after evaporating solvent. ^{1}H NMR (CDCl$_3$, ppm): 7.47 (d, 2H), 7.37, 7.23 (m, 20H), 5.96 (s, 2H), 1.43 (s, 2H). ^{13}C NMR (CDCl$_3$, ppm): δ 143.6, 140.9, 140.4, 140.2, 129.5, 128.8, 128.7, 128.3, 128.2, 127.3, 126.7, 72.4. Anal. Calcd: C, 86.85; H, 5.92. Found: C, 86.43; H, 5.96.

6,12-Diphenyl-6,12-dihydroindeno[1,2-*b*]fluorene (IV) or m-3. 5.39 g of BF$_3$·Et$_2$O was added dropwise to a solution of 0.74 g of compound **III** in 200 mL of methylene chloride. The resulting solution was stirred at room temperature for 20 min. Ethanol (10 mL) was added, followed by 150 mL of water. The organic layer was separated and washed with water

and dried over $MgSO_4$, and the solvent then was evaporated. The crude product was purified by flush column (methylene chloride as eluent). This reaction gave a quantitative yield of compound **IV**. ^{1}H NMR ($CDCl_3$, ppm): 7.67 (d, 4H), 7.33−7.08 (m, 16H), 5.07 (s, 2H). ^{13}C NMR ($CDCl_3$, ppm): δ 148.7, 148.0, 142.2, 141.4, 141.1, 129.2, 128.9, 127.7, 127.5, 127.3, 125.7, 120.2, 117.2, 54.7. Anal. Cacld: C, 94.55; H, 5.45. Found: C, 92.79; H, 5.66.

P-3-8. 1.30 mL of butyllithium (2.0 M solution in cyclohexane) was added dropwise to a solution of compound **IV** (0.50 g) in 20 mL of THF at 0 °C. The mixture was kept at this temperature and reacted for 45 min. 0.335 g of 1,8-dibromooctane in 10 mL of THF was added slowly to the reacting mixture and stirred for a further 24 h. The polymer was precipitated by adding large amounts of methanol, gathered by filtration, and washed extensively by methanol. 0.53 g of pale yellow polymer was obtained. ^{1}H NMR ($CDCl_3$, ppm): 7.58 (b, 2H); 7.48 (b, 2H); 7.18 (m, 16H); 2.40 (4H); 1.03−0.71 (b, 12H). ^{13}C NMR ($CDCl_3$, ppm): 152.7, 151.8, 145.6, 141.1, 140.9, 128.7, 127.6, 127.2, 126.7, 124.7, 120.1, 116.0, 58.9, 38.5, 30.4, 29.7, 24.3. Anal. Calcd: C, 92.98; H, 7.02. Found: C, 91.19; H, 7.02.

P-3-6. The synthetic procedure was same as for **P-3-8.** Anal. Calcd: C, 93.40; H, 6.60. Found: C, 91.42; H, 6.37. ^{1}H NMR ($CDCl_3$, ppm): 7.50 (m, 4H); 7.18 (m, 16H); 2.30 (b, 4H); 1.09 (b, 4H); 0.68 (b, 4H).

P-3-5. The synthetic procedure was same as for **P-3-8.** Anal. Calcd: C, 93.54; H, 6.46. Found: C, 92.05; H, 6.43. ^{1}H NMR ($CDCl_3$, ppm): 7.50 (m, 4H); 7.20 (m, 16H); 2.30 (b, 4H); 1.09 (b, 4H); 0.74 (b, 2H).

P-3-4. The synthetic procedure was same as **P-3-8.** Anal. Calcd: C, 93.63; H, 6.37. Found: C, 92.35; H, 6.47. ^{1}H NMR ($CDCl_3$, ppm): 7.52 (m, 4H); 7.13 (m, 16H); 2.29 (b, 4H); 0.78 (b, 4H).

2-Bromo-9,9-dihexylfluorene. 4.90 g of 2-bromofluorene was reacted with *n*-hexyl bromide in a two-phase system composed of 45 mL of toluene and 45 mL of 50 wt % sodium hydroxide aqueous solution using tetrabutylammonium bromide as the phase transfer catalyst as 60 °C for 5 h. After diluting the reaction mixture with ethyl acetate, the organic layer was washed by water and dried over $MgSO_4$. The crude product was purified by flash column (hexane as eluent) and gave 7.99 g (yield: 97%) of pure product. ^{1}H NMR ($CDCl_3$, ppm): 7.65 (m, 1H), 7.54 (d, 1H), 7.44 (dd, 2H), 7.31 (d, 3H), 1.92 (m, 4H), 1.09 (m, 12H), 0.76 (t, 6H), 0.59 (p, 4H). ^{13}C NMR ($CDCl_3$, ppm): δ 153.3, 150.7, 140.5, 140.4, 130.3, 127.9, 127.3, 126.5, 123.3, 121.4, 121.3, 120.1, 55.8, 40.7, 31.9, 30.0, 24.1, 23.0, 14.4.

2-Borodihydroxy-9,9-dihexylfluorene (V). To a solution of 2-bromohexylfluorene (5.91 g) in 30 mL of THF at −78 °C was added dropwise 11.6 mL of butyllithium (2.0 M in cyclohexane). The mixture was stirred at −78 °C for 45 min, and then this reaction mixture was transferred dropwise to another flask containing 14.5 mL of isopropyl borate in 30 mL of THF. The resulting mixture was warmed to room temperature for 24 h. The mixture was hydrolyzed by 50 mL of 2 N HCl for 30 min. The organic layer was separated and washed with brine and dried over $MgSO_4$. After evaporating the solvent, the residue was purified by pouring into cold hexane. 4.96 g of white precipitate can be obtained (yield: 63%). ^{1}H NMR (THF-d_8, ppm): 7.83 (s, 2H); 7.77 (d, 1H); 7.11 (dd, 1H); 7.67 (d, 1H); 7.36 (dd, 1H); 7.26 (dd, 2H); 2.02 (t, 4H); 1.07 (m, 12H); 0.79 (t, 6H); 0.64 (p, 4H). ^{13}C NMR (THF-d_8, ppm): 151.3, 149.5, 143.5, 141.8, 133.1, 128.4, 128.2, 127.4, 126.9, 123.0, 120.1, 118.8, 55.1, 50.0, 40.8, 31.9, 30.1, 22.9, 13.7.

2,5-Bis(9,9-dihexyl-9*H*-fluoren-2-yl)benzene-1,4-dicarbaldehyde The procedure was the same as that of compound **II**. ^{1}H NMR ($CDCl_3$, ppm): 10.12 (s, 2H), 8.21 (s, 2H), 7.84 (d, 2H), 7.78 (dt, 2H), 7.43 (dd, 2H) 7.38 (m, 8H), 2.02 (m, 8H), 1.13 (m, 24H), 0.77 (t, 12H), 0.67 (m, 8H). ^{13}C NMR ($CDCl_3$, ppm): δ 192.4, 151.9, 151.4, 145.3, 142.2, 140.5, 137.2, 135.4, 130.6, 129.4, 128.1, 127.4, 125.0, 123.4, 120.5, 120.3, 55.7, 40.7, 31.9, 30.1, 24.2, 23.0, 14.4. Anal. Calcd: C, 87.17; H, 8.83. Found: C, 86.87; H, 8.83.

[2,5-Bis(9,9-dihexyl-9*H*-fluoren-2-yl)-4-(hydroxyphenylmethyl)phenyl]phenylmethanol. The procedure was

the same as that of compound **III**. ^{1}H NMR ($CDCl_3$, ppm): 7.72 (m, 2H), 7.58 (s, 2H), 7.35 (m, 4H), 7.28−7.20 (m, 18H), 6.07 (s, 2H), 1.90 (m, 8H), 1.48 (b, OH), 1.16−1.04 (m, 24H), 0.75 (t, 12H), 0.67 (m, 8H). ^{13}C NMR ($CDCl_3$, ppm): δ 150.9, 150.7, 143.8, 141.2, 140.7, 140.3, 140.1, 139.2, 129.1, 128.3, 128.2, 127.4, 127.1, 126.8, 126.7, 124.0, 122.9, 119.8, 119.4, 72.6, 55.1, 40.3, 31.5, 29.8, 23.9, 22.6, 14.0. Anal. Calcd: C, 88.00; H, 8.65. Found: C, 87.71; H, 8.68.

Pentamer, m-5. The procedure was the same as that of compound **IV**. ^{1}H NMR ($CDCl_3$, ppm): 7.76 (s, 2H), 7.64 (s, 2H), 7.58 (d, 4H), 7.41−7.22 (m, 16H), 5.17 (s, 2H), 1.99 (t, 8H), 1.14−1.04 (m, 24H), 0.75 (t, 12H), 0.63 (m, 8H). ^{13}C NMR ($CDCl_3$, ppm): δ 151.0, 150.6, 148.1, 147.3, 142.3, 141.1, 140.7, 140.6, 128.8, 128.7, 126.9, 126.6, 122.8, 119.4, 116.4, 114.1, 54.8, 54.1, 40.7, 31.5, 29.7, 23.8, 22.6. Anal. Calcd: C, 91.45; H, 8.55. Found: C, 91.30; H, 8.45.

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