Synthesis and Characterization of Alternating Copolymers of Fluorene and Oxadiazole

Jianfu Ding,* Michael Day, Gilles Robertson, and Jacques Roovers

Institute for Chemical Process and Environmental Technology, National Research Council Canada, 1200 Montreal Road, Building M-12 Ottawa, Ontario, Canada, K1A 0R6

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ABSTRACT: Alternating copolymers of 9,9-dioctylfluorene and oxadiazole have been prepared by the tetrazole route or the Suzuki coupling reaction. In the polymers the oxadiazole units were evenly dispersed in the main chain at every one, P(F_1-*alt*-Ox), three, P(F_3-*alt*-Ox), or four, P(F_4-*alt*-Ox), fluorene units. Another copolymer with an asymmetric repeat unit structure, P(F_3−Ox−F_1−Ox) has also been prepared for comparison. In this study, the tetrazole route has been demonstrated to offer several advantages for preparing polyoxadiazole with well-defined structures compared to other oxadiazole ring formation reactions. These advantages include: clean and fast reactions, mild reaction conditions, high yields, and high molecular masses of product. The glass transition temperature of copolymers ranged from 98 to 150 °C, and the copolymers show high thermal stability with decomposition temperatures around 430 °C. The UV−vis absorption and photoluminescence properties of all the copolymers in solutions are similar to those of poly(9,9-dioctylfluorene). All copolymers fluoresce in the blue-light range with quantum yields of ~70% in CH_2Cl_2 solution.

Introduction

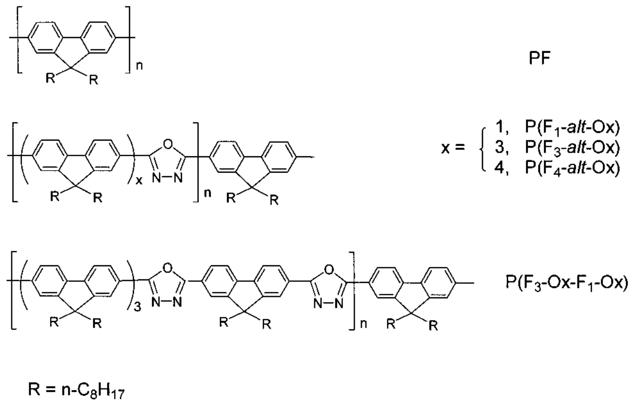
The first demonstration of efficient polymer light-emitting diodes (PLEDs) in 1990[1] stimulated a great interest in display applications for conjugated semiconducting polymers.[2,3] Compared to conventional LEDs, PLEDs offer a wide variety of advantages. For instance, they are much easier to process and can be fabricated into large flat panel displays.

Among the three primary colors, green[4] and red[5] PLEDs have been successfully fabricated with high efficiency. Meanwhile the performance of blue devices needs to be improved.[2e] Because blue-light emissions are associated with higher energy gaps, higher electric field intensities have to be applied to the light-emitting layer. Consequently higher thermal and oxidative stabilities are demanded for the blue light-emitting polymers.

Polymers of fluorene present an interesting approach to blue-light-emitting polymers due to their high chemical stability and the versatile chemical structures, which make them ideal for chemical modification.[2a] Polymerizations of fluorene monomers with various comonomers by Suzuki coupling[3] or Yamamoto coupling[6] reactions have yielded a wide range of copolymers. Many of these materials show good photoluminescence efficiency and in some cases high thermal and oxidative stability. The facile functionallisation at the 9-position of fluorene also offers the ability to control interchain interaction, cross-linking ability and electrical and optical properties.

To obtain high efficient PLED devices, a balance in the injection of holes and electrons into the polymer emissive layer is necessary. However, for most conjugated polymers developed so far, the injection and transport of electrons are much less efficient than those of holes. Therefore, attention has been drawn to the development of polymers with improved electron transporting capability.[2b,7,8] Conjugated polymers with high electron affinities have lower barriers for electron injection from metal cathodes.[2d,9] Polymers containing electron-withdrawing units in the main chain or at side groups usually have high electron affinities. Copolymers containing 1,3,4-oxadiazole have been found to be very efficient at increasing electron affinity and as a result are capable of enhancing their electron transporting properties.[2b,8] In addition by conjugated with phenyl ring, oxadiazole units show blue-light-emitting behavior.[10b] Of equal importance, the presence of these units in copolymers has been observed to enhance the thermal and oxidative stability.[10]

Scheme 1. Chemical Structure of the Polymers



In this work, two types of copolymers of 9,9-dioctylfluorene with oxadiazole have been prepared: one with a symmetric structure of repeat units and the other with an asymmetric structure. Their structures are shown in Scheme 1. In the symmetric polymers, the oxadiazole units were evenly dispersed in the main chain, at every one, three, or four fluorene units. In the asymmetrically structured copolymer the oxadiazole units were dispersed in the manner as shown in Scheme 1. Both types of polymers have well-defined chain structures. The purpose of this study was to prepare copolymers with different oxadiazole content and different symmetry in order to determine the effect of oxadiazole unit and chain regularity on performance of the polymers includ-

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* To whom correspondence should be addressed.

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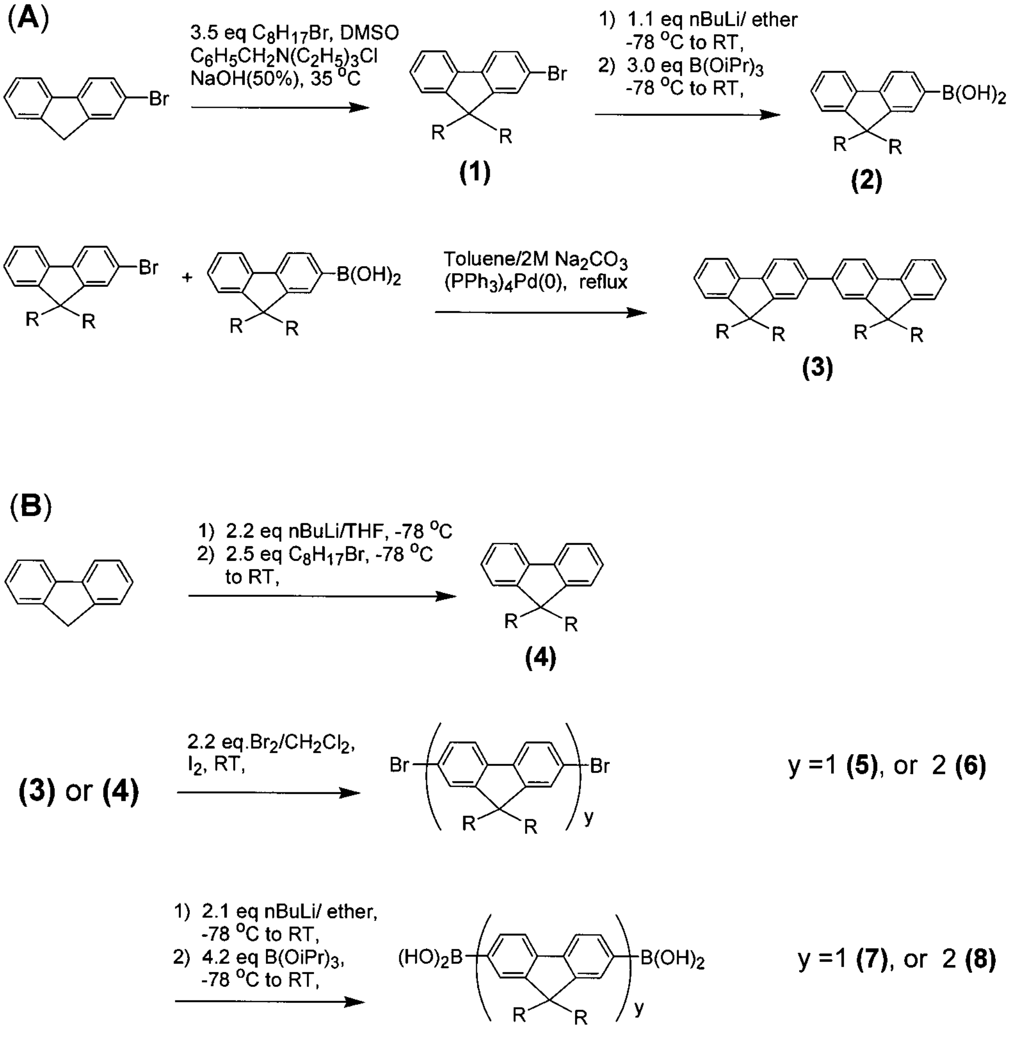
Scheme 2. Preparation of Diboronic Acid of 9,9-Dioctyfluorene and Bis(9,9-dioctyl)fluorene



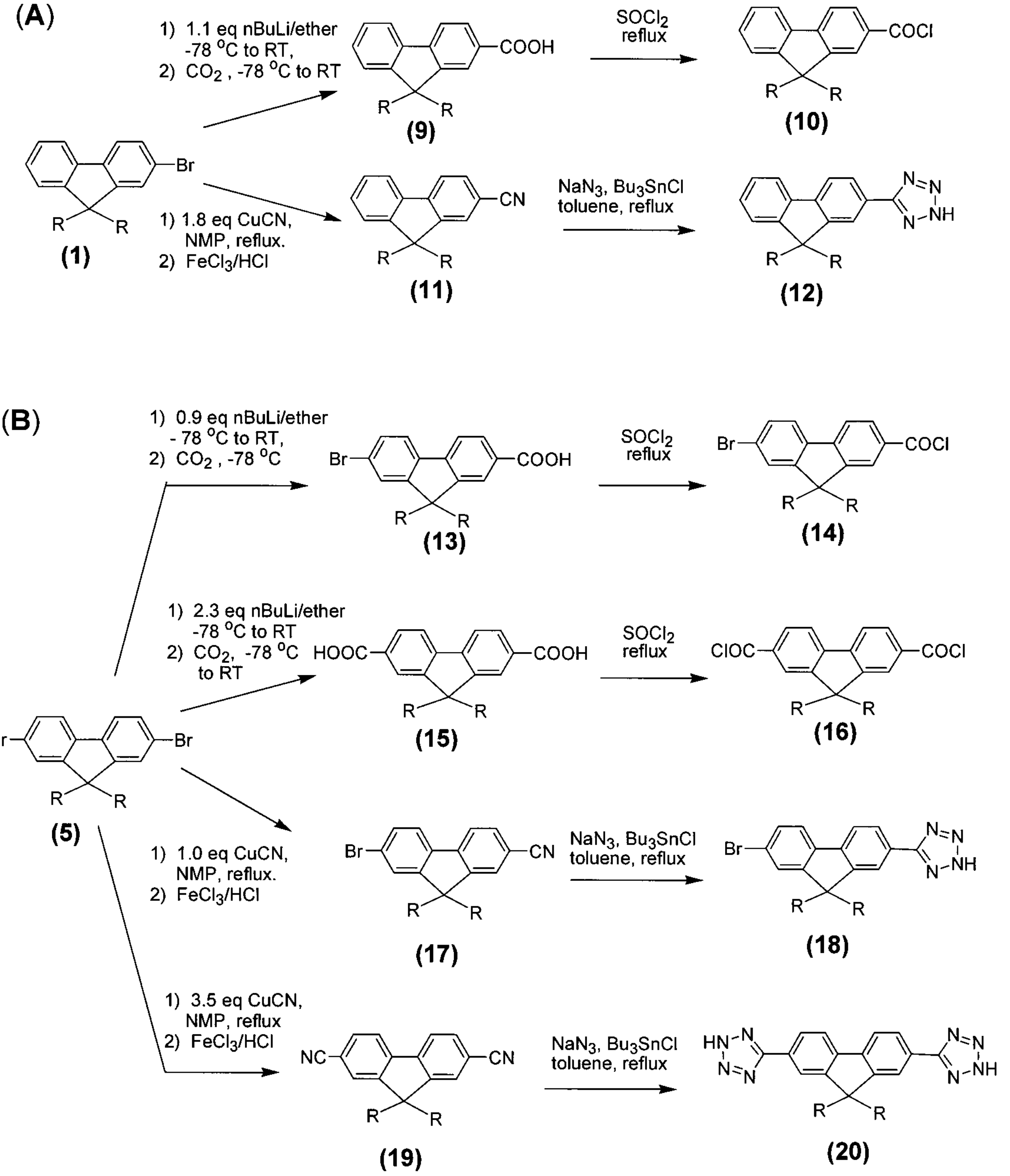
ing stability, charge transport, and electroluminescent efficiency.[3a] For a similar reason, a homopolymer of 9,9-dioctylfluorene has been also prepared by the Suzuki coupling reaction using an A−B type monomer.[11] Electrochemical characterization as well as photo- and electroluminescent studies demonstrated excellent stabilities for the majority of the copolymers at both positive and negative charged states and very stable blue-light-emitting properties. Electrochemical studies also showed that the insertion of oxadiazole units into polyfluorene chain brought the electron affinities of the copolymers close to the work functions of the cathodes (Ca, Mg). All the results indicated the copolymers are good candidate materials for an electron transport layer in polymer blue-light-emitting diodes. The relevant results will be published separately.[12]

Results and Discussion

Monomer Synthesis. The synthetic approach used in this study started with fluorene and 2-bromofluorene (Scheme 2). The hydrogens on the 9-position of 2-bromofluorene are sufficiently acidic to react with 1-bromooctane when catalyzed by concentrated NaOH aqueous solution (50% w/w) in the presence of a phase transfer catalyst, $C_6H_5CH_2N(C_2H_5)_3Cl$.[13] This reaction affords 2-bromo-9,9-dioctylfluorene (**1**) in a high yield (95%). The main byproduct of this reaction is the monosubstituted material that can be removed by column chromatography with hexane. 2,7-Dibromofluorene reacts in a similar manner to afford 2,7-dibromo-9,9-dioctylfluorene (**5**). However a more traditional route involving lithiation was chosen to prepare **5** from fluorene (Scheme 2B).[3a−c] This reaction affords a product with higher purity. Because both hydrogens in the 9-position of fluorene can be completely deprotonated by *n*-BuLi, only traces of monosubstituted byproduct are formed in this reaction. After bromination, the crude product is easily purified by recrystallization with hexane to produce white crystals with an overall yield of 85% for this two-step reaction. The bromination of **4** was catalyzed by trace I_2.[3c] Some other catalysts such as $FeCl_3$, or Pd/C were also reported for this reaction.[3a,6c,14] However, we found that I_2 gave higher yields and higher purity.

The bromide (**1**, **5** or **6**) was converted to the boronic acid (**2**, **7**, or **8**) by lithiating the compound in diethyl ether at low temperatures, followed by reaction with $B(OiPr)_3$.[13b,15] The resulting boronate was then hydrolyzed with 2 N HCl to give the boronic acid with yields from 55% to 76%. The low yields associated with this reaction were due to the loss of product during purification. It was for this reason that boronic esters rather than the acid were used by some other researchers.[3a−b] The use of $B(OMe)_3$ was also investigated instead of $B(OiPr)_3$; however, the yield was much lower (<20%).

Scheme 3. Chemistry of 2-Bromo-9,9-dioctylfluorene (A) and 2,7-Dibromo-9,9-dioctylfluorene (B)

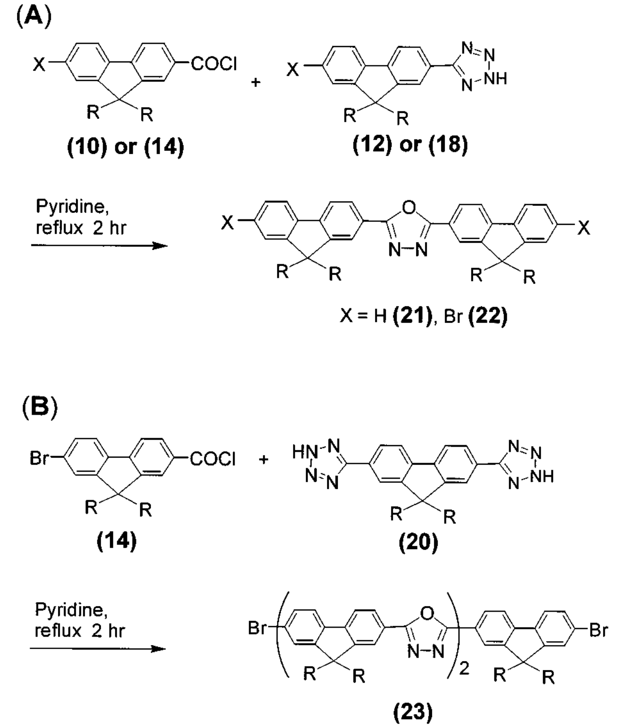


Bis(9,9-dioctylfluorene) (**3**) was prepared by the Suzuki coupling reaction of boronic acid **2** with bromide **1**.[11,16] Several coupling reactions including Grignard,[17] Yamamoto,[6] Stille,[3c,18] and Negishi[19] reactions were investigated for the formation of the C—C bond between the aromatic rings in the preparation of the conjugated oligomers and polymers. In this work, it was found that the Suzuki coupling reaction was the most favorable. The advantages associated with this reaction scheme include[20] reactivity less sensitive to steric hindrance, mild reaction conditions, reactions less sensitive to the presence of function groups and the environment, less side reactions, and higher conversions.

Bromides **1** and **5** were also used for the preparation of the carboxylic chloride and tetrazole (Scheme 3), which were used as the starting materials in the oxadiazole ring formation. In the reaction of dibromide **5** with *n*-BuLi, the first formed C—Li bond deactivates the second bromo-group, and allows the reaction to be easily controlled at the monosubstituted level. Therefore, the monocarboxylic (**13**) and dicarboxylic (**15**) compounds can be prepared in high yield by controlling the molar ratio of **5**/*n*-BuLi at 1.0/1.0 and 1.0/2.1, respectively. However, from a practical point of view, a molar ratio of **5**/*n*-BuLi of l/0.9 was preferred for preparing monocarboxylic product since it benefits the product purification. The unreacted dibromide was easily removed from the product by column chromatography, while the bicarboxylic byproduct, which is formed when excess *n*-BuLi was used, was very difficult to remove.

A different situation arose when carbonitrile derivatives (**17** and **19**) were prepared from **5**. The reactivities of the first and the second bromo groups in **5** are very similar for this reaction, and the ratio of monosubstituted product to disubstituted product was found to be 6/4 (from NMR measurements of the reaction mixture). Therefore, the yield of monosubstituted product was

Scheme 4. Formation of the Oxadiazole Ring

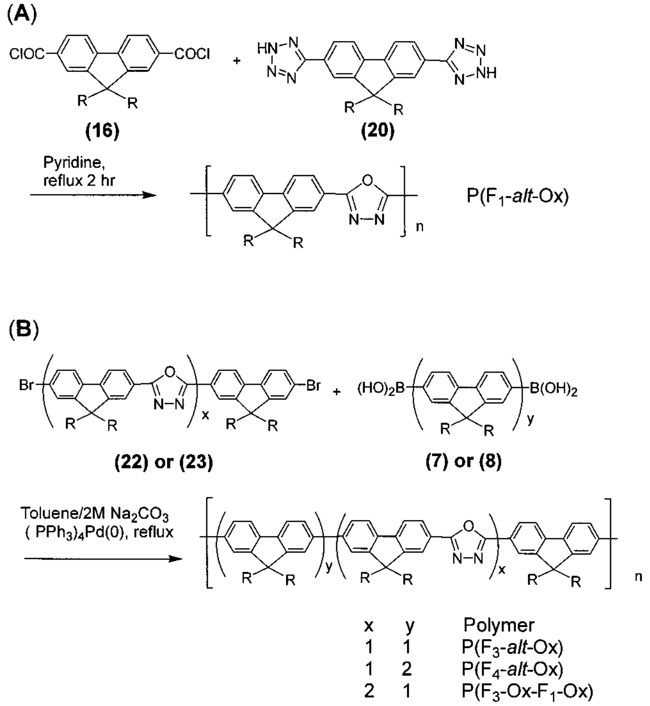


always low (<60%). Fortunately, the separation of the monosubstitute product from disubstituted product was easily achieved by column chromatography, and both products are useful materials in this study.

Tetrazole compounds (**12**, **18**, and **20**) were prepared from the corresponding carbonitrile derivatives by reacting with Bu_3SnCl and NaN_3.[21] This reaction route was chosen due to its low sensitivity to the presence of functional groups (Br in this work) in comparison to other synthetic routes.[22] For all three products, the yields were low (35–64%). The reason for the low yields has been attributed to the product being formed in salt form that proved difficult to recover during purification.

Oxadiazole formation is described in Scheme 4. Because of the high thermal and chemical stability associated with oxadiazole compounds along with their good electron transporting properties,[8,10] a large amount of work has been devoted to investigating the synthesis of oxadiazole containing monomers and polymers. Three reaction schemes have been extensively studied.[10b] The first involves the dehydration of hydrazides with phosphorus oxychloride or other dehydrating agents.[8a–c,10a,23] The second is a one-step polycondensation reaction, which involves reacting the carboxylic acid and hydrazine sulfate in a strong acid.[10a,24] The third route involves the condensation of tetrazole with carboxylic chloride under mild condition.[22,25] Although the first two reactions have been widely used for preparing oxadiazole-containing polymers, they do pose some problems. The main disadvantages are associated with side reactions,[22b,24c] which lead to impurities and end groups that are covalently bound to the polymer, which cannot be easily removed during subsequent purification. This caused the formation of defects in the structure, which are responsible for poor performance of the product as a light-emitting material. Essentially, the defects quench the fluorescence and enhance the polymer degradation. However, the condensation between tetrazole and carboxylic chloride are clean and fast with high yields under mild reaction conditions.

Scheme 5. Preparation of Copolymers Using the Tetrazole Route (A) and by the Suzuki Reaction (B)



Another important advantage of the tetrazole route is that the reaction is unaffected by functional groups such as bromine in the starting material. These features therefore made this procedure ideal for the preparation of 1,3,4-oxadiazole containing monomers with versatile structures, which could be used in subsequent coupling polymerization reactions such as the Suzuki and Yamamoto reaction. In this study the dibromide of trimer, Br–F–Ox–F–Br (**22**), and pentamer, Br–F–Ox–F–Ox–F–Br (**23**), have been prepared.

Polymerization by the Tetrazole Route (Scheme 5A). The tetrazole route was first used in polymerizations in 1961.[25a] However it was reported that only low molecular mass polymers were obtained from this reaction, and therefore, little attention was given to apply this reaction to prepare polymers in the past few decades.[10b,27] However, this reaction does exhibit several advantages in comparison to the other two reactions as mentioned above. The most important advantages are that side reactions are minimized and high yields are possible (73–96% in this work). The tetrazole route was therefore applied to the polycondensation of 9,9-dioctylfluorene-2,7-ditetrazole (**20**) with 9,9-dioctylfluorene-2,7-dicarboxylic chloride (**16**) (see Scheme 5A). An aromatic polyoxadiazole (PF_1-*alt*-Ox) with well-defined structure was obtained in a high yield (93%). The molecular mass was also sufficiently high (M_n = 12.0 kDa), and compared favorably with other well-developed polycondensation reactions.[16–20] The end group in this polymer could be carboxylic acid or tetrazole. The resulting polymer was pale yellow in color and soluble in most common solvent such as toluene, chloroform and THF. This result demonstrated the high potential to prepare polyoxadiazoles with high molecular mass by the tetrazole route.

Polymerization by the Suzuki Reaction (Scheme 5B). On the other hand, polyoxadiazoles with different composition were prepared from oxadiazole containing dibromide **22**, which copolymerized with diboronic acid

Table 1. Molecular Weight of the Polymers

polymer	M_n (kDa)	M_w (kDa)	PDI	DP	polymerization (monomer type)
PF	7.9	13.7	1.73	20.3	Suzuki (A−B)
P(F_1-*alt*-Ox)	12.0	27.3	2.28	26.3	tetrazole route (A−A, B−B)
P(F_3-*alt*-Ox)	25.1	62.8	2.50	20.4	Suzuki (A−A, B−B)
P(F_4-*alt*-Ox)	30.4	82.0	2.70	18.8	Suzuki (A−A, B−B)
P(F_3−Ox−F_1−Ox)	21.6	56.7	2.63	12.8	Suzuki (A−A, B−B)

7 or **8** by the Suzuki coupling reaction to offer P(F_3-*alt*-Ox), or P(F_4-*alt*-Ox), respectively. Similarly, P(F_3−Ox−F_1−Ox) was prepared from **23** and **7**. In all these reactions, the diboronic acid was carefully dried under high vacuum (10^{-3} mmHg) and was correctly weighed to obtain an equimolar ratio of diboronic acid/dibromide in the feed. The end group of the polymers was not controlled in this reaction and therefore it could be either bromide or boronic acid.

Traces of Pd(II) formed from the Pd(0) catalyst used in the Suzuki reaction can form a complex with the oxadiazole units in the resulting polymers[26] and cause the polymers to darken in color. Attempts to remove the residual catalyst using common extracting methods recommended for many Suzuki reactions[3a−b,16] were unsuccessful. The polymer was therefore purified by precipitating the reaction mixture into an acid solution (concentrated HCl/methanol/acetone, 1:2:2 by volume). Light colored polymers were obtained using this approach. The polymers were then washed with water and methanol and finally extracted with acetone. The resulting polymer was then dried under high vacuum.

So far, alternating copolymers of fluorene and oxadiazole with F/Ox ratios of 1/1 have been prepared by the tetrazole route, the copolymers with 3/1 and 4/1 ratios, and the asymmetric copolymer (F/Ox = 2) have been prepared by the Suzuki coupling reaction.

Molecular Mass. Polystyrene equivalent GPC molecular masses of the polymers prepared using these two approaches are given in Table 1. All the polymers gave high quality films by spin-coating from dichloromethane solution. Table 1 shows that the M_n of the copolymer prepared by the tetrazole route is slightly lower than those of the polymers obtained using the Suzuki reaction. Because the formula weights of the repeat units are different for each polymer, it can be misleading to use molecular mass alone as an indicator for the extent of conversion. The degree of polymerization (DP) is related to the average number of new bonds formed in each polymer during reaction. For condensation polymerization, it is therefore an indicator of the degree of conversion. The value of DP in Table 1 indicates that the oxadiazole ring formation from tetrazole has a higher conversion than that from the Suzuki reaction.

^{1}H NMR and ^{13}C NMR of Copolymers. The ^{1}H NMR spectra of the copolymers are presented in Figure 1. Three groups of peaks associated with chemical shifts at 8.20−8.24 (a), 7.88−7.96 (b), and 7.69 (c) can be attributed to aromatic protons. The assignment of these peaks is given in Figure 1. In addition, P(F_3-*alt*-Ox) displays some small peaks in the same region, which may originate from end groups or are caused by traces of residual Pt(II). However, P(F_1-*alt*-Ox) has a quite clean spectrum, indicating that the tetrazole route is capable of producing a purer polymer with well-defined structure.

An interesting phenomenon is found in the alkyl region (0.5−2.5 ppm) of the copolymers. The protons on the second methylene of octyl side group are located on the top of a conjugated plane of fluorene and are shielded by the π-electrons of the fluorene ring, and consequently, their resonance appears at higher field in the spectrum.[3b] The chemical shift is 0.60 ppm for the trimer (**21**) and 0.61 ppm for the pentamer (**23**) (see Experimental Section). However, it increases to 0.66 ppm for P(F_1-*alt*-Ox), and further increases with the length of fluorene segment in the repeat units of the polymers. It reaches 0.79 ppm for P(F_4-*alt*-Ox). This phenomenon was explained by the increased delocalization of π-electron with the increased length of the oligomer chain and the increased length of the fluorene segment in the repeat units of the polymers.

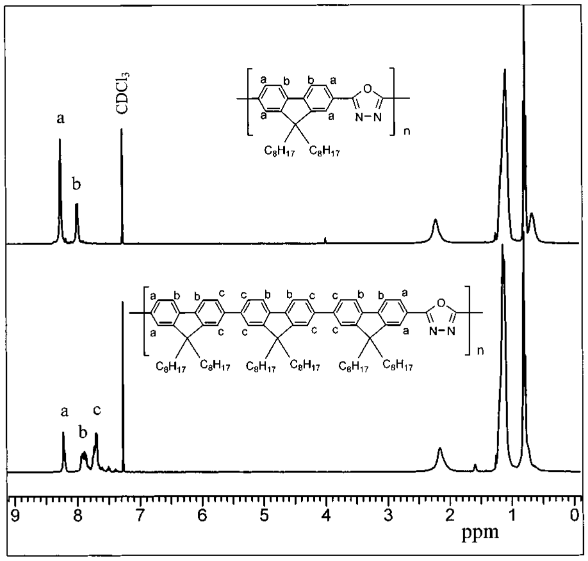


Figure 1. ^{1}H NMR spectra of the copolymers of fluorene and oxadiazole.

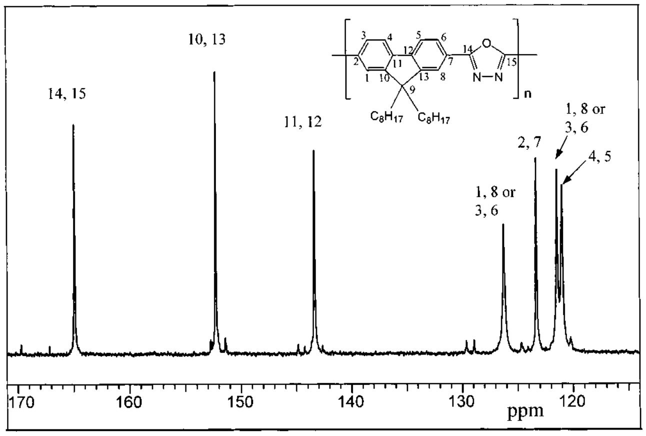


Figure 2. Aromatic region of the ^{13}C NMR spectrum of P(F_1-*alt*-Ox) in $CDCl_3$.

In the carbon NMR of P(F_1-*alt*-Ox) (shown in Figure 2), only seven carbon peaks appear in the region related to 14 aromatic atoms of the symmetric unit. Three absorptions peaks are at lower field than ordinary aromatic carbons. One of them, the aromatic carbon of the oxadiazole ring, is bonded to two electron-withdrawing atoms and is therefore expected to resonate at very low field. The other two are from the four aromatic carbons of the cyclopentadiene structure of the fluorene group. Because of the rigid five-member ring structure, those four aromatic carbons are subjected to the ring current effect of the opposite benzene ring and are

Table 2. Characteristics of the Polymers

polymer	T_g (°C)	T_d[a] (°C)	λ_{abs}[b] (nm)	λ_{PL}[b] (nm)	ϕ_{PL}[c]
PF	51		384	415 (439)	0.75
P(F$_1$-*alt*-Ox)	150	439	394 (372)	402 (426)	0.73
P(F$_3$-*alt*-Ox)	114	431	396 (380)	420 (442)	0.75
P(F$_4$-*alt*-Ox)	98	432	395 (381)	422 (443)	0.72
P(F$_3$−Ox−F$_1$−Ox)	127	430	396 (379)	422 (444)	0.67

[a] Temperature of 1% weight loss measured by TGA in nitrogen. [b] Wavelength of maximum absorbance or emission, wavelength of the shoulder peak is in brackets. [c] Photoluminescence quantum yield in CH_2Cl_2 (λ_{exc} = 375 nm).

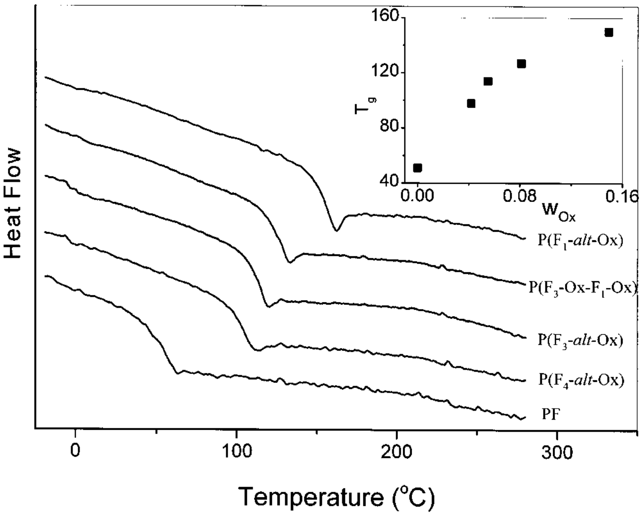


Figure 3. DSC thermograms of copolymers of fluorene and oxadiazole and polyfluorene. (insert) a plot of T_g vs weight content of oxadiazole (w_{Ox}) of the copolymers.

therefore deshielded and also appear at lower field. With the help of one-bond and three-bond heteronuclear correlation, as well as the spectra of the monomer (**21**), it is possible to assign the hydrogen and carbon peaks as shown in the figures. Some small peaks were also found in the aromatic region of the carbon spectrum. These may originate from terminal groups. The integration of these peaks showed the intensity of the small peaks is only 2−4% of the intensity of the normal peaks. This information once again confirmed the well-defined structure of P(F$_1$-*alt*-Ox).

Thermal Properties. The thermal properties of the polymers were investigated by DSC and TGA under flowing nitrogen conditions. The relevant data are reported in Table 2. The glass transition temperature (T_g) was measurement on the second heating curve (Figure 3) after the sample had first been heated to 250 °C and then allowed to slowly cool to room temperature. No first-order transitions were detected in the DSC thermograms for all 5 polymers in the region from −20 to +280 °C. The T_g of the copolymer with 1:1 molar ratio of F/Ox is 150 °C. This value decreased with the decreasing of oxadiazole content as displayed in the insert of Figure 3. The decomposition temperatures (T_d), as measured by TGA, were all around 430 °C. The fact that no obvious difference of T_d was noted due to oxadiazole content, suggests that both fluorene and oxadiazole units in the polymer are equally thermal stable and are not subject to neighbor effects.

Optical Properties. Figure 4 presents the UV−vis absorption and photoluminescence (PL) spectra of the copolymers along with polyfluorene and trimer **21** for comparison. Because the spectra of P(F$_3$−Ox−F$_1$−Ox), P(F$_4$-*alt*-Ox) and P(F$_3$-*alt*-Ox) are almost identical, only the spectra of P(F$_3$-*alt*-Ox) have been displayed in Figure 4, while the data are summarized in Table 2. The emission spectra for all polymers were measured in CH_2Cl_2 solution using excitation at 375 nm, along with that of 9,10-diphenylanthracene, a standard material for quantum yield analysis. The emission spectrum of trimer **21** was excited at 344 nm, the wavelength of the maximum absorption.

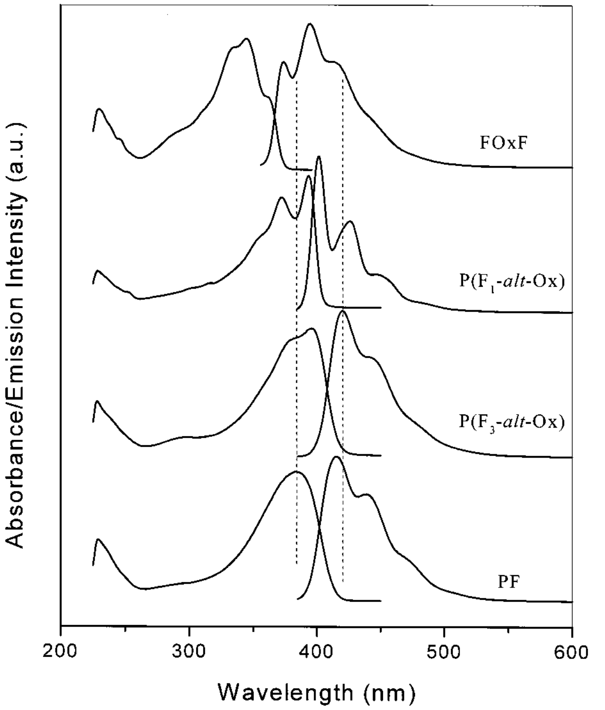


Figure 4. Absorption and emission spectra of trimer (FOxF), polyfluorene, and the copolymers.

The UV−vis and PL spectra of the copolymers were all very similar to those of polyfluorene, except for P(F$_1$-*alt*-Ox). From the results it appears that as oxadiazole units are inserted into the polyfluorene conjugated chain, there is a 10−12 nm red-shift in the absorption spectra and 5−7 nm red-shift in emission spectra, and the extent of the red-shift was not affected by the oxadiazole content in the chain. This observation suggests that the oxadiazole unit does not cause interruption of the main chain conjugation as suggested by Lee for PPV type copolymers.[29] This observation also appears to be applicable to P(F$_1$-*alt*-Ox). Its absorption spectrum displays a vibronic fine structure with two sharp bands at 372 and 394 nm, which are close to those reported for the other copolymers, once again suggesting that the conjugate length is not affected by the increased oxadiazole units in the chain. This hypothesis, was further examined by comparing the absorption spectrum of P(F$_1$-*alt*-Ox) with those of oligomers with analogous chain structures as shown in Figure 5. In this case, an increase in chain length caused a bathochromical shift with a maximum absorption occurring at 345 nm for FOxF (**21**), 348 nm for BrFOxFBr (**22**), 363 nm for BrFOxFOxFBr (**23**), and 394 nm for P(F$_1$-*alt*-Ox). This result indicates that the conjugate length increased with the chain length of the oligomers and confirms that the oxadiazole units in the main chain do not interrupt the conjugation of the copolymers. A similar phenomenon was also reported for the oxadiazole containing poly(phenylenevinylene).[30]

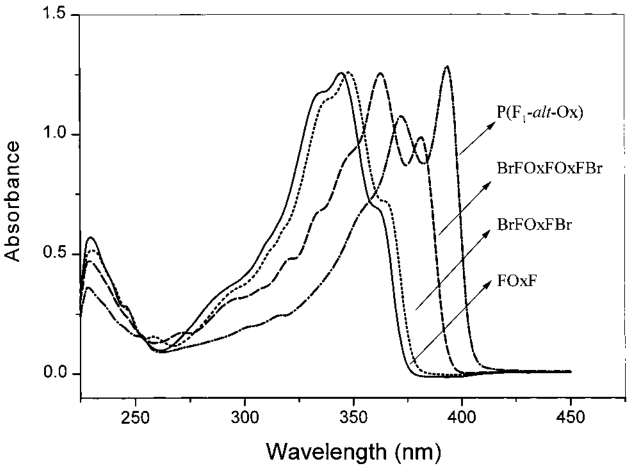


Figure 5. Absorption spectra of trimer **21**, dibromotrimer **22**, dibromopentamer **23**, and P(F_1-*alt*-Ox).

Experimental Section

Instrumentation. Nuclear magnetic resonance spectra were recorded on a Varian Unity Inova spectrometer at a resonance frequency of 399.961 MHz for ^{1}H and 100.579 MHz for ^{13}C. Carbon spectra of polymers as well as carbon hydrogen correlations were obtained using a 10 mm tunable broadband probe with one-bond $^1J_{C-H}$ set to 120 Hz while long-range three-bond $^3J_{C-C-C-H}$s were set to 7.5 Hz. Molecular masses [number-average (M_n) and weight-average (M_w)] were determined by size exclusion chromatography (SEC) with a Waters 515 HPLC pump and a Waters 410 differential refractometer. The instrument was calibrated with polystyrene standards in THF (HPLC grade). Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed using a purged nitrogen atmosphere at a heating rate of 10 °C/min, using TA Instruments 951 and 910 modules, respectively, controlled by a 2100 controller. The glass transition temperature (T_g) was recorded on the second heating curve. The melting point range (mp) was recorded from the interval between the onset and the maximum of the endothermic peak obtained from the first heating curve. Absorption and photoluminescence (PL) emission spectra of the polymers were measured in dichloromethane (HPLC grade) using a Hewlett-Packard 8453 spectrophotometer and a Spex Fluorolog 3 spectrometer, respectively. The fluorescence analysis was performed using about 10^{-6} M solutions. Quantum yields were determined using argon saturated solutions in dichloromethane and were calculated by comparing emission with that of a standard solution of 9,10-diphenylanthracene in cyclohexane ($\phi_{PL} = 0.95$) at room temperature.[28] Elemental analyses were conducted on a LECO CHNS932 analyzer.

Materials. All starting materials and reagents were purchased from Aldrich. All the solvents for characterization were used as received without further purification. The solvents for chemical reaction were dried under the protection of argon. THF was refluxed with K/Na alloy in the presence of benzophenone until a persistent blue color appeared and then distilled. Diethyl ether and toluene were refluxed with Na for 4 h and then distilled. Dichloromethane was refluxed with CaH_2 and distilled.

Synthesis. 9,9-Dioctylfluorene (4). This material was prepared using a method similar to that in ref 3a. A 2.5 M *n*-butyllithium solution (264 mL, 660 mmol, in hexane) was added dropwise to a solution of fluorene (49.9 g, 300 mmol) in 600 mL of anhydrous THF at −78 °C. The mixture was stirred at −78 °C for 45 min, and then 1-bromooctane (144.8 g, 750 mmol) was added dropwise followed by further stirring at −78 °C for 1 h. The solution was then allowed to slowly warm to room temperature and stirred for another 1 h. Then 500 mL aqueous NH_4Cl solution (10%, w/w) was added with stirring. The organic layer was separated and washed twice with 500-mL aliquots of water before being dried over anhydrous $MgSO_4$. The solvent was then removed under reduced pressure followed by the removal of excess of 1-bromooctane by distillation under vacuum (2 mmHg) at 100 °C (bath temperature). The product (pale yellow oil) was directly used without further purification. ^{1}H NMR, δ ($CDCl_3$): 7.68 (d, $J = 6.8$ Hz, 2H), 7.30 (m, 6H), 1.94 (m, 4H), 0.96−1.24 (m, 20H), 0.81 (t, $J = 7.2$ Hz, 6H), 0.60 (m, 4H). Anal. Calcd for $C_{29}H_{42}$: C, 89.16; H, 10.84. Found: C, 88.56; H, 10.38.

2,7-Dibromo-9,9-dioctylfluorene (5).[3c] Bromine (159.6 g, 660 mmol) in CH_2Cl_2 (100 mL) was slowly added with stirring at room temperature to a CH_2Cl_2 (600 mL) solution of the above product (**4**) (300 mmol) containing I_2 (0.12 g, 0.47 mmol). This is an exothermic reaction, and any rapid addition of the bromine should be avoided. The solution was stirred at room temperature for 20 h in the dark, and 300 mL of aqueous $NaHSO_3$ (15%) was added. Vigorous stirring was applied until the red color disappeared (<30 min). The organic layer was separated, washed with water and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the product was purified by recrystallization from hexane three times to yield a white crystalline product. The overall yield of these two reactions was 85.4%. Mp: 51.0−53.7 °C. ^{1}H NMR, δ ($CDCl_3$): 7.51 (dd, $J = 7.6$ Hz, 1.0 Hz, 2H), 7.44 (dd, $J = 7.6$ Hz, 1.6 Hz, 2H), 7.43 (s, 2H), 1.90 (m, 4H), 0.98−1.24, (m, 20H), 0.82 (t, $J = 7.2$ Hz, 6H), 0.57 (m, 4H). Anal. Calcd for $C_{29}H_{40}Br_2$: C, 63.51; H, 7.35. Found: C, 62.18; H, 8.07.

2-Bromo-9,9-dioctylfluorene (1).[13] A mixture of 2-bromofluorene (24.5 g, 100 mmol) and benzyltriethylammonium chloride (1.36 g) in 80 mL of DMSO and 40 mL of aqueous NaOH (50%, w/w) was purged with argon. 1-Bromooctane (67.6 g, 350 mmol) was added to the mixture using a syringe. The resulting solution was stirred at 35 °C for 5 h before 80 mL of H_2O was added. The solution was then extracted twice with 100 mL of diethyl ether. The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure, followed by removal of excess 1-bromooctane by distillation under vacuum. The crude product was purified by column chromatography using hexane as eluent to yield a colorless oil in 95% yield. ^{1}H NMR, δ ($CDCl_3$): 7.65 (m, 1H), 7.54 (dd, $J = 7.2$ Hz, 1.5 Hz, 1H), 7.44 (s, 1H), 7.43 (dd, $J = 7.6$ Hz, 1.8 Hz, 1H), 7.31 (m, 3H), 1.92 (m, 4H), 0.97−1.24 (m, 20H), 0.81 (t, $J = 7.2$ Hz, 6H), 0.58 (m, 4H). Anal. Calcd for $C_{29}H_{41}Br$: C, 74.18; H, 8.80. Found: C, 74.56; H, 8.85.

9,9-Dioctylfluorene-2,7-diboronic Acid (7).[11a,b,15a] A 2.5 M solution of *n*-butyllithium (42 mL, 105 mmol) was added to an argon-purged solution of (**5**) (27.4 g, 50 mmol) in anhydrous diethyl ether (300 mL) at −78 °C using a syringe. The solution was then allowed to slowly warm to room temperature, and stirred for a further1 h before it was cooled again to −78 °C. Triisopropyl boronate (39.5 g, 210 mmol) was added with a syringe. The resulting mixture was once again allowed to warm to room temperature and was stirred for an additional 20 h (vigorous stirring was required during this step to avoid gel formation). Then 2 N HCl (200 mL) was added to the stirred solution while maintaining the solution at room temperature for 1 h. The organic layer was separated and the water layer was extracted with 200 mL of diethyl ether. The combined ether layers were washed twice with 200 mL of water. The solvent was then removed under reduced pressure. The crude product was purified by Soxhlet extraction with hexane to give a white powder in a yield of 65%. Mp: >400 °C dec. ^{1}H NMR, δ (CD_3OD): 7.74 (m, 4H), 7.59 (s, 2H), 2.00 (m, 4H), 0.94−1.24 (m, 20H) 0.80 (t, $J = 7.2$ Hz, 6H), 0.52 (m, 4H). Anal. Calcd for $C_{29}H_{44}O_4B_2$: C, 72.83; H, 9.27. Found: C, 73.21; H, 9.87.

9,9-Dioctylfluorene-2-boronic Acid (2). This compound was prepared using a similar procedure to that used for **7** starting with compound **1**. **1** was reacted with *n*-BuLi, and then (iPrO)$_3$B, using molar ratios of 1.0:1.1:3.0. The crude product was purified by column chromatography using AcOEt/hexane (30/70, v/v) as eluent to yield a white powder in 55% yield. Mp: 70.1−77.3 °C.^{1}H NMR, δ ($CDCl_3$): 8.31 (dd, $J = 7.6$ Hz, 1.0 Hz, 1H), 8.22 (s, 1H), 7.89 (d, $J = 7.6$ Hz, 1H), 7.81 (m, 1H), 7.38 (m, 3H), 2.09 (m, 4H), 0.97−1.22 (m, 20H), 0.77

(t, J = 7.2 Hz, 6H), 0.68 (m, 4H). Anal. Calcd for $C_{29}H_{43}O_2B$: C, 80.17; H, 9.98. Found: C, 81.04; H, 9.75.

2,2′-Bis(9,9-dioctylfluorene) (3).[11,15] **1** (9.36 g, 20.0 mmol) and **2** (8.68 g, 20.0 mmol) were mixed in toluene (120 mL), and 2 M Na_2CO_3 (80 mL) was added. The mixture was purged with argon. $(PPh_3)_4Pd^0$ (0.23 g, 0.20 mmol) was then added in a glovebox. The mixture was refluxed with stirring in the dark for 48 h under the protection of argon. The organic layer was then separated and washed with water and dried with $MgSO_4$. The solution was then filtered through silica gel to remove the dark color. The solvent was removed under reduced pressure. The crude product was purified by recrystallization first from hexane and then from acetone to give pale-green needlelike crystals in a yield of 81%. Mp: 74.3−79.2 °C. ^1H NMR, δ ($CDCl_3$): 7.76 (d, J = 7.8 Hz, 2H), 7.73 (dd, J = 7.8 Hz, 2H), 7.63 (dd, J = 8.0 Hz, 1.6 Hz, 2H), 7.60 (d, J = 1.4 Hz, 2H), 7.32 (m,6H), 2.01 (m, 8H), 0.99−1.24 (m, 40H), 0.80 (t, J = 7.2 Hz, 12H), 0.70 (m, 8H). Anal. Calcd for $C_{58}H_{82}$: C, 89.39; H, 10.61. Found: C, 89.63; H, 10.27.

2,2′-Bis(7-bromo-9,9-dioctylfluorene) (6). This material was prepared in a manner similar to that used for **5**. **3** was reacted with Br_2 using a molar ratio of **3**/Br_2 of 1.0:2.2. The resulting product was twice recrystallized from acetone to give white crystals in a yield of 86.7%. Mp: 58.5−64.9, 74.5−78.8 °C (bimodal), ^1H NMR, δ ($CDCl_3$): 7.73, (d, J = 8.0 Hz 2H), 7.61 (dd, J = 8.0 Hz, 1.6 Hz, 2H), 7.58 (dd, J = 7.6 Hz, 1.0 Hz, 2H), 7.47 (s, 2H), 7.46 (dd, J = 7.6 Hz, 1.6 Hz, 2H), 1.99 (m, 8H), 0.99−1.23 (m, 40H), 0.80 (t, J = 0.76 Hz, 12H), 0.68 (m, 8H). Anal. Calcd for $C_{58}H_{80}Br_2$: C, 74.34; H, 8.61. Found: C, 72.78; H, 8.88.

2,2′-Bis(9,9-dioctyl)fluorene-7,7′-diboronic Acid (8). This material was prepared in a procedure similar to that used for **7**. **6** was reacted with *n*-BuLi followed by $(iPrO)_3B$ using molar ratios of 1.0:2.1:4.2. The crude product was purified by recrystallization from hexane twice to give a white powder in 76% yield. Mp: 124.9−127.1−136.3 °C (bimodal). ^1H NMR, δ ($CDCl_3$/acetone-d_6): 8.01 (s, 2H), 7.92 (d, J = 8.0 Hz, 4H), 7.86 (d, J = 1.7 Hz, 2H), 7.82 (dd, J = 7.6 Hz, 0.7 Hz, 2H), 7.76 (dd, J = 7.6 Hz, 1.7 Hz, 2H), 2.14 (m, 8H), 1.00−1.24 (m, 40H), 0.78 (t, J = 7.2 Hz, 12H), 0.69 (m, 4H). Anal. Calcd for $C_{58}H_{84}O_4B_2$: C, 80.36; H, 9.98. Found: C, 81.19; H, 9.47.

2,7-Dicyano-9,9-dioctylfluorene (19).[20,22a] A mixture of **5** (15.0 g, 27.3 mmol) and CuCN (8.58 g, 95.8 mmol) in NMP (80 mL) was purged with argon and refluxed for 4 h. The hot reaction mixture (~120 °C) was then slowly poured into a stirred acidified aqueous $FeCl_3$ solution (60.0 g of $FeCl_3$ in 15 mL of concentrated HCl and 90 mL of H_2O). The mixture was stirred for a further 20 min at 90 °C. The aqueous layer was then separated from the organic layer and was extracted with toluene (120 mL) twice. The combined organic layer was washed with 100 mL of 6 N HCl until the dark heavy organic layer disappeared. The organic layer was then washed with water, 10% NaOH solution, and water again prior to being dried over $MgSO_4$. The solution was filtered to remove insoluble particles. The solvent was then removed under reduced pressure to give a crude product. The crude product was purified by column chromatography using AcOEt/hexane (20/80, v/v) as eluent, followed by recrystallization from hexane to offer colorless crystals in a yield of 73%. Mp: 77.5−79.7 °C, ^1H NMR, δ ($CDCl_3$): 7.82 (dd, J = 8.0 Hz, 0.7 Hz, 2H), 7.68 (dd, J = 8.0 Hz, 1.4 Hz, 2H), 7.64 (m, 2H), 1.99 (m, 4H), 0.97−1.26 (m, 20H), 0.82 (t, J = 7.2 Hz, 6H), 0.51 (m, 4H). Anal. Calcd for $C_{31}H_{40}N_2$: C, 84.49; H, 9.15; N, 6.36. Found: C, 83.30; H, 10.23; N, 6.38.

7-Bromo-9,9-dioctylfluorene-2-carbonitrile (17). This material was prepared using a similar procedure to that used for **19**, starting from **5** using an equimolar ratio of **5**/CuCN. The crude product was purified by column chromatography using AcOEt/hexane (10/90, v/v) as eluent to give a white powder with a yield of 45%. Mp: 48.3−52.2 °C, ^1H NMR, δ ($CDCl_3$): 7.72 (dd, J = 8.0 Hz, 0.6 Hz, 1H), 7.62 (dd, J = 8.0 Hz, 1.4 Hz, 1H), 7.59 (dd, J = 7.2 Hz, 1.6 Hz, 1H), 7.57 (m, 1H), 7.50 (dd, 7.2 Hz, 1.8 Hz, 1H), 7.49 (s, 1H), 1.94 (m, 4H), 0.97−1.26 (m, 20 H), 0.81 (t, J = 7.2 Hz, 6H), 0.53 (m, 4H). Anal. Calcd for $C_{30}H_{40}BrN$: C, 72.86; H, 8.15; N, 2.83. Found: C, 73.65; H, 8.80; N, 2.55.

9,9-Dioctylfluorene-2-carbonitrile (11). This material was prepared using a similar procedure as that used for **19**. **1** was reacted with CuCN in a molar ratio of 1:1.8. The crude product was purified by column chromatography using AcOEt/hexane (7/93, v/v) as eluent to produce a pale yellow oil in a yield of 81%. ^1H NMR, δ ($CDCl_3$): 7.75 (dd, J = 8.0 Hz, 0.7 Hz, 1H), 7.73 (m, 1H), 7.62 (dd, J = 8.0 Hz, 1.5 Hz, 1H), 7.59 (s, 1H), 7.37 (m, 3H), 1,96 (m, 4H), 0.96−1.23 (m, 20H), 0.80 (t, J = 7.2 Hz, 6H), 0.53 (m, 4H). Anal. Calcd for $C_{30}H_{41}N$: C, 86.69; H, 9.94; N, 3.37. Found: C, 85.57; H, 9.59; N, 3.23.

9,9-Dioctylfluorene-2,7-ditetrazole (20).[22] A mixture of **19** (12.0 g, 27.3 mmol) and NaN_3 (4.29 g, 65.5 mmol) in anhydrous toluene (60 mL) was purged with argon. $(n\text{-}Bu)_3SnCl$ was added to the mixture using a syringe. The mixture was refluxed for 24 h. The solution was then acidified with concentrated HCl, and washed with water (100 mL) three times. The suspended solid was collected by filtration and purified by column chromatography using AcOEt/hexane (33/67,v/v) followed by acetone as eluent. This gave a product in a yield of 35%. Mp: 120.5−134.0 °C. ^1H NMR, δ ($CDCl_3$/acetone-d_6): 8.19 (d, J = 1.2 Hz, 2H), 8.11 (dd, J = 8.0 Hz, 1.2 Hz, 2H), 7.93 (d, J = 8.0 Hz, 2H), 2.09 (m, 4H), 0.89−1.13 (m, 20H), 0.69 (t, J = 7.2 Hz, 6H), 0.59 (m, 4H). Anal. Calcd for $C_{31}H_{42}N_8$: C, 70.69; H, 8.04; N, 21.27. Found: C, 70.03; H, 8.46; N, 20.79.

7-Bromo-9,9-dioctylfluorene-2-tetrazole (18). This compound was prepared using a similar procedure as that for **20**. **17** was reacted with NaN_3 in a molar ratio of 1:1.2. After the crude product was recovered from the reaction mixture by filtration, it was washed with hexane and methanol twice respectively to give a white powder in a yield of 64%. Mp: 179.9−182.7 °C.^1H NMR, δ ($CDCl_3$/acetone-d_6): 8.13 (d, J = 1.5 Hz, 1H), 8.06 (d, J = 8.0 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.50 (d, J = 1.8 Hz, 1H), 7.45 (dd, J = 8.0 Hz, 1.8 Hz, 1H), 2.01 (m, 4H), 0.91−1.18 (m, 20H), 0.73 (t, J = 7.2 Hz, 6H), 0.56 (m, 4H). Anal. Calcd for $C_{30}H_{41}BrN_4$: C, 67.03; H, 7.69; N, 10.42. Found: C, 68.37; H, 7.86; N, 10.55.

9,9-Dioctylfluorene-2-tetrazole (12). This material was prepared using a similar procedure as that for **20**. **11** was reacted with NaN_3 in a molar ratio of 1:1.1. After the reaction mixture was acidified and washed with water, the solvent was removed under reduced pressure. The crude product was purified by column chromatography using a mixture of AcOEt/hexane (40/60, v/v) as an eluent to give a pure product in a yield of 58%. ^1H NMR, δ ($CDCl_3$): 8.11 (d, J = 1.4 Hz, 1H), 8.04 (d, J = 8.0 Hz,1H), 7.79 (dd, J = 8.0 Hz, 1H), 7.68 (m, 1H), 7.36 (m, 3H), 2.02 (m, 4H), 0.90−1.16 (m, 20H), 0.76 (t, J = 7.2 Hz, 6H), 0.57 (m, 4H). Anal. Calcd for $C_{30}H_{42}N_4$: C, 78.56; H, 9.23; N, 12.22. Found: C, 77.63; H, 9.15; N, 12.03.

9,9-Dioctylfluorene-2,2-dicarboxylic Acid (15). A solution of *n*-BuLi (23.5 mL, 58.8 mmol) was added dropwise into an argon-purged solution of **5** (14.0 g, 25.5 mmol) in anhydrous diethyl ether (200 mL) at −78 °C. The solution was then allowed to warm to room temperature with stirring for 1 h before it was cooled back to −78 °C. CO_2 dried with 3 Å molecular sieves was bubbled into the slurry over a period of 1 h while maintaining the temperature at −78 °C. The slurry was then allowed to slowly warm to room temperature with stirring and maintained for a further 1 h before being acidified with 2 N HCl solution (120 mL). The organic layer was then separated and washed with water and the solvent removed under reduced pressure. The crude product was purified by recrystallization from acetone to give a white powder with a yield of 90%. Mp: 218.8−222.2 °C. ^1H NMR, δ ($CDCl_3$/acetone-d_6): 8.04 (dd, J = 8.0 Hz, 1.5 Hz, 2H), 8.02 (m, 2H), 7.78 (dd, J = 8.0 Hz, 0.7 Hz, 2H), 1.99 (m, 4H), 0.89−1.16 (m, 20 H). 0.72 (t, J = 7.2 Hz, 6H), 0.49 (m, 4H). Anal. Calcd for $C_{31}H_{42}O_4$: C, 77.79; H, 8.84. Found: C, 78.34; H, 8.76.

7-Bromo-9,9-dioctylfluorene-2-carboxylic Acid (13). This material was prepared using a similar procedure to that used for **15**. **5** was reacted with *n*-BuLi in a molar ratio of 1:0.9. The resulting crude product was purified by column chromatography using AcOEt/hexane (5/95) followed by AcOEt/hexane

(20/80) to give a white powder with a yield of 65%. Mp: 113.3−116.4 °C. ^{1}H NMR, δ ($CDCl_3$): 8.13 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 8.06 (d, J = 1.6 Hz, 1H). 7.74 (dd, J = 8.0 Hz, 0.5 Hz, 1H), 7.62 (d, J = 8.4 Hz, 1H), 7.50 (d, J = 1.8 Hz, 1H), 7.49 (dd, J = 8.4 Hz, 1.8 Hz, 1H), 1.98 (m, 4H), 0.97−1.25 (m, 20H), 0.80 (t, J = 0.72 Hz, 6H), 0.57 (m, 4H). Anal. Calcd for $C_{30}H_{41}BrO_2$: C, 70.16; H, 8.05. Found: C, 71.47; H, 8.04.

9,9-Dioctylfluorene-2-carboxyl Acid (9). This material was prepared using a similar procedure to that used for **15**. **5** was reacted with *n*-BuLi in a molar ratio of 1:1.1. The crude product was purified by column chromatography using AcOEt/hexane (5/95) followed by AcOEt/hexane (20/80), prior to recrystallization from hexane to give a white powder with a yield of 73%. Mp: 55.7−61.4 °C. ^{1}H NMR, δ ($CDCl_3$): 8.13 (dd, J = 8.0 Hz, 1.5 Hz, 1H), 8.08 (d, J = 1.5 Hz, 1H), 7.77 (m, 2H), 7.37 (m, 3H), 2.00 (m, 4H), 0.95−1.24 (m, 20H), 0.80 (t, J = 0.72 Hz, 6H), 0.58 (m, 4H). Anal. Calcd for $C_{30}H_{42}O_2$: C, 82.90; H, 9.74. Found: C, 82.88; H, 9.58.

BrF−Ox−FBr, Dibromotrimer 22.[22b,c] A solution of **13** (8.15 g 16.4 mmol) in $SOCl_2$ (80 mL) was refluxed for 4 h under argon to convert the acid to the corresponding acid chloride (**14**). The excess $SOCl_2$ and other volatile materials were then distilled off under reduced pressure. Then 20 mL anhydrous pyridine was added to the green solid to give a solution that was added dropwise to a solution of **18** (8.00 g, 14.9 mmol) in anhydrous pyridine (40 mL) using a syringe. The resulting mixture was refluxed for 2 h under argon and was cooled to room temperature prior to being poured into methanol with stirring to precipitate the product. The crude product was purified by chromatography using AcOEt/hexane (5/95) followed by AcOEt/hexane (15/85). White crystals in a yield of 96% were obtained on recrystallization from acetone. Mp: 109.5−113.8, 134.3−136.5 °C (double peak). ^{1}H NMR, δ ($CDCl_3$): 8.13 (dd, J = 7.6 Hz, 1.6 Hz, 2H), 8.12 (s, 2H), 7.81 (dd, J = 7.6 Hz, 1.3 Hz, 2H), 7.63 (d, J = 8.4 Hz, 2H), 7.51 (d, J = 1.8 Hz, 2H), 7.50 (dd, J = 8.1 Hz, 1.8 Hz, 2H), 2.03 (m, 8H), 0.96−1.23 (m, 40H), 0.78 (t, J = 7.2 Hz, 12H), 0.60 (m, 8H). Anal. Calcd for $C_{60}H_{80}Br_2N_2O$: C, 71.70; H, 8.02; N, 2.79. Found: C, 72.77; H, 7.98; N, 2.76.

F−Ox−F, Trimer 21. This trimer was prepared using a similar procedure as that for **22** starting from **9** and **12** with an equimolar ratio of **9**/**12**. The resultant crude product was purified by recrystallization from hexane to give a white crystalline product in a yield of 77%. Mp: 128.6−131.3 °C. ^{1}H NMR, δ ($CDCl_3$): 8.15 (s, 2H), 8.14 (dd, J = 7.2 Hz, 1.6 Hz, 2H), 7.84 (dd, J = 7.2 Hz, 1.6 Hz, 2H), 7.77 (m, 2H), 7.38 (m, 6H), 2.05 (m, 8H), 0.96−1.23 (m, 40H), 0.78 (t, J = 7.2 Hz, 12H), 0.61 (m, 8H). Anal. Calcd for $C_{60}H_{82}N_2O$: C, 85.05; H, 9.76; N, 3.31. Found: C, 85.94; H, 9.76; N, 3.29.

BrF−Ox−F−Ox−FBr, Dibromopentamer 23. This compound was prepared using a similar procedure as that used for **22** starting from **13** and **20**. The molar ratio of **13**/**20** was 3.0:1.0. The resulting crude product was purified by chromatography using AcOEt/hexane (5/95) followed by AcOEt/hexane (15/85), Recrystallization from AcOEt/hexane (10/90) gave white crystals with a yield of 81%. Mp: 110.9−120.9. ^{1}H NMR, δ ($CDCl_3$): 8.199 (dd, J = 8.4 Hz, 1.6 Hz, 2H), 8.197 (d, J = 1.6 Hz, 2H), 8.15 (dd, J = 8.0 Hz, 1.5 Hz, 2H), 8.14 (s, 2H), 7.94 (d, J = 8.4 Hz, 2H), 7.84 (dd, J = 8.0 Hz, 0.8 Hz, 2H), 7.64 (d, J = 8.4 Hz, 2H), 7.513 (d, J = 1.8 Hz, 2H), 7.509 (dd, J = 8.4 Hz, 1.8 Hz, 2H), 2.17 (m, 4H), 2.04 (m, 8H), 0.97−1.23 (m, 60H), 0.79 (t, J = 7.2 Hz, 12H), 0.75 (t, J = 7.2 Hz, 6H), 0.61 (m, 12H). Anal. Calcd for $C_{91}H_{120}Br_2N_4O_2$: C, 74.77; H, 8.28; N, 3.83. Found: C, 75.77; H, 7.96; N, 3.81.

Polymerization. (a) By the Tetrazole Route. P(F_1-*alt*-Ox) was prepared using a procedure similar to that used for the preparation of **22**. The reaction involves converting dicarboxylic acid **15 (**2.00 g, 4.18 mmol) to dicarboxylic chloride **16** and then reacting with ditetrazole **20** (2.15 g, 4.08 mmol) with an equimolar ratio of **15**/**20**. The resulting polymer, P(F_1-*alt*-Ox), was recovered from the reaction solution by precipitating into methanol/acetone (1:1) and collected by filtration. The isolated polymer was purified by dissolving in THF and reprecipitating into methanol/acetone (1/1). The polymer was then dried under high vacuum to give 3.48 g of a pale yellow powder with a yield of 93%.

(b) By the Suzuki Coupling Reaction. All the other polymers were prepared using a procedure similar to that used for preparing **3**. The reactions involved starting with 2.00 g of the relevant dibromide, **22** or **23**, and diboronic acid, **7** or **8**, at an equimolar ratio. Once the reaction was completed, the organic layer was separated, and added dropwise with stirring to a mixture of concentrated HCl/methanol/acetone (0.5:1:1). The resulting polymer was recovered by filtration, washed with methanol, and further purified by dissolving in toluene and reprecipitating into methanol/acetone (1/1) mixture. The polymer was then extracted with acetone for 48 h and dried under high vacuum to give the products (pale green in color) with the following yields: P(F3-*alt*-Ox), 2.33 g, 95%; P(F4-*alt*-Ox), 2.90 g, 90%; P(F3−Ox−F−Ox), 2.08 g, 90%.

Conclusion

In this paper, we have established synthetic approaches to the preparation of copolymers of fluorene and oxadiazole with well-defined structure using the tetrazole route and the Suzuki coupling reaction. Both methods yield high molecular mass polymers with minimum side reactions. All the polymers exhibit good thermal behavior and stability. The absorption and emission spectra of the polymer solutions revealed that the oxadiazole ring in the polymer could form a good conjugation with fluorene and offer the polymers excellent fluorescence properties as blue-light-emitting materials.

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