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Novel conjugated polymers containing fluorene and 1-(2-benzothiazolyl)-3,5-diphenylpyrazoline Unit with Efficient Photoluminescence

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Summary

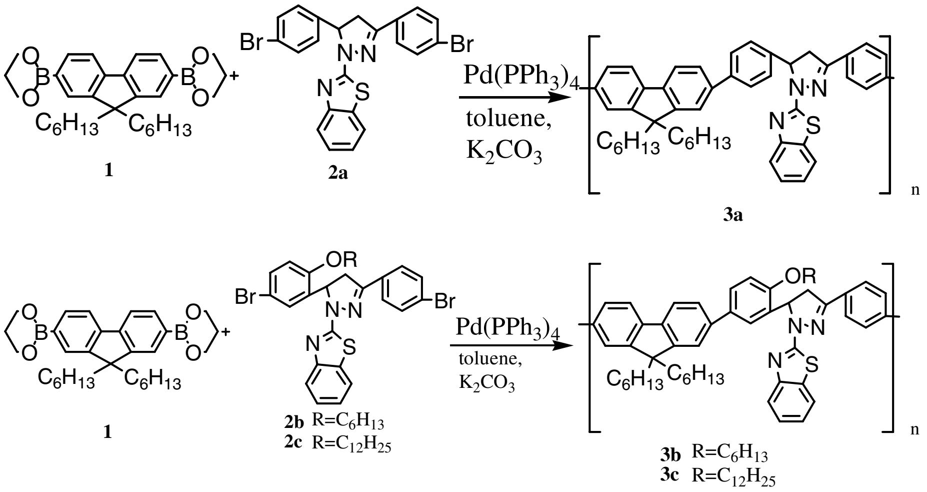
Novel conjugated polymers based on fluorene having 1-(2-benzothiazolyl)-3, 5-diphenylpyrazoline unit in the main chain were synthesized in good yields through Suzuki coupling reactions. All polymers were quite soluble in a variety of organic solvents. Transparent and uniform thin films of the polymers were obtained easily by casting or spin-coating from toluene solution. These polymers possessed satisfactory thermal stability. The polymers exhibited strong bluish-green photoluminescence in solution and green photoluminescence in the solid state.

Introduction

Since the discovery of polymer light-emitting diodes (PLEDs) by the Cambridge group in 1990[1], EL conjugated polymers have attracted much interest because of their potential application in large-area flat-panel displays [2, 3]. A large number of electroactive and photoactive conjugated polymers have been introduced during the past few years, such as poly(p-phenylenevinylene)(PPV), poly(p-phenylene)(PPP), polythiophene(PT) and polyfluorene(PF), etc.[3-5]. Among these polymers, PLEDs based on polyfluorene showed exceptional optoelectronic properties because they contained a rigid planar biphenyl unit and facile substitution at the remote C-9 position, which improved the solubility and processability of the polymer without significantly increasing the steric interactions in the polymer backbone[6]. As a result, polyfluorenes have emerged as very promising candidates for PLEDs due to their high fluorescence quantum yield, excellent film-forming and good thermal stability[7-18]. However, there are some issues that need to be resolved with PFs and their derivatives. A major problem in obtaining electroluminescence (EL) from PFs is the long wavelength tail in the emission spectra. It is caused by the formation aggregated and the formation of interchain excimers, which leads to the problem of color purity of light emitted from the fabricated PLEDs. To prevent π stacking between polymer chains and to suppress the formation of excimers in the solid state, bulky substituted groups, such as Quinoline, quinoxaline and oxadiazole were introduced into the main chain of PFs [19-26]. But most of these units are electron-deficient moieties, which can easily form trapping centers that reduce the fluorescence quantum efficiencies of the polymers. Therefore, it is a major challenge to find suitable conjugated polymers with excellent color purity and high quantum efficiencies.

Triarylpyrazoline compounds have been widely used as fluorescent brightening agent in the textile industry due to their excellent fluorescence[27]. There is a heterocyclic ring in the structure of pyrazoline containing two nitrogen atoms, one of which form an electron–donating p-π conjugated system, so it is able to function as hole-transporting materials used in OLED[28]. These compounds exhibit twisted intramolecular charge transfer(TICT)[29]. Upon excitation, Triarylpyrazolines with TICT will twist, and some specific conformation will form in the electron donor-accepter system , which can strengthen molecules' fluorescence. And their excellent fluorescent property makes it possible to be used as emitting materials in OLED[30,31].

However, the films of small molecular pyrazolines were inferior and tend to crystallize after film formation, which lead to device degradation. The reason is that the pyrazolines monomers have low melt point [28]. In this paper, we synthesized a series of novel fluorene-based conjugated polymers containing 1-(2-benzothiazolyl)-3,5-diphenylpyrazoline in the backbone to solve this problem and to increase polymers' quantum yield as well.



Scheme 1

Experimental

Materials

All the chemicals were purchased from Aldrich or Acros chemical company and were used without any further purification. All the solvents such as DMF and toluene were dried with appropriate drying agents, then distilled under reduced pressure. The Catalyst $Pd(PPh_3)_4$ [32], 9,9-dihexylfluorene-2,7-bis(trimethyleneboronates) **1** [13], 1-(2-benzothiazolyl)-3,5-bis(4-bromophenyl)-4,5-dihydro-1-H-pyrazole **2a** [33], 1-(2-benzothiazolyl)-3-(4-bromophenyl)-5-(2-hexyloxyl-5-bromophenyl)-4,5-dihydro-1-H-pyrazole **2b** [33] and 1-(2-benzothiazolyl)-3-(4-bromophenyl)-5-(2-dodecyloxyl-5-

bromophenyl)-4,5-dihydro-1-H-pyrazole **2c** [33] were prepared following the already published procedures.

Measurements

^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Unity INOVA-400 and Bruker AC-200 spectrometer. The FT-IR spectra were obtained on a Perkin-Elmer 2000 infrared spectrometer as KBr pellets. UV-Vis spectra of the polymers in solutions and as thin films were taken on a Suhimadzu UV2100 UV-Vis recording spectrometer. Photoluminescence (PL) spectra of the polymers in solutions and thin films were measured on a Hitachi 850 fluorescence spectrometer. Thermal gravimetric analysis (TGA) measurements were performed on Perkin-Elmer series 7 thermal analysis system under N_2 at a heating rate of 10 °C min^{-1}. Differential scanning calorimetry(DSC)measurements were performed on a Perkin-Elmer DSC 7 under N_2 at a heating rate of 10 °C min^{-1}. The weight-average molecular weights(M_w) and polydispersity indices(M_w /M_n) of the polymers were measured on a PL-GPC model 210 chromatograph at 25 °C, using THF as the eluent and standard polystyrene as the reference.

Polymerization

A typical procedure is as follows. To a mixture of **1**, **2a** (0.513 g,1.0mmol) and Pd(PPh_3)$_4$ (12 mg, 0.01 mmol) was added a mixture of toluene (5mL)and aqueous 2M potassium carbonate(5mL). The mixture was vigorously stirred at 85-90 °C for 48 h under Ar. After the mixture was cooled down to room temperature, it was poured into 200 mL of methanol and deionized water (v:v, 10:1). A fibrous solid was obtained by filtration, the solid was washed with methanol, water and then methanol. After washing for 24 h in a Soxhlet apparatus with acetone, polymer **3a** was obtained as a yellow powder with yield of 84% after drying under a vacuum.

3a:.^{1}H NMR(400 MH$_Z$, $CDCl_3$) δ 7.89-7.10(m, 18H, ph-H), 5.91(m, 1H, pyrazoline CH), 4.03, 3.41(m, 2H, pyrazoline CH_2), 2.16-0.72(m, 26H, alyl-H); ^{13}C NMR (50 MH$_Z$, $CDCl_3$) δ 163.2, 152.5, 152.2, 151.9, 151.7, 151.6, 143.0, 141.1, 140.6, 140.4, 140.1, 139.9, 139.7, 139.4, 139.1, 138.9, 131.8, 129.9, 129.9, 128.9, 127.6, 127.3, 126.9, 126.5, 125.9, 125.6, 121.8, 121.3, 120.7, 120.1, 63.7, 63.5, 55.3, 43.7, 40.3, 31.4, 30.3, 29.6, 23.8, 22.5, 13.9. IR (KBr pellet) 1601.4 cm^{-1}(s, C=N).

3b: Yild:85%; ^{1}H NMR(400 MH$_Z$, $CDCl_3$) δ 8.15-6.86(m, 17H, ph-H), 6.02(m, 1H, pyrazoline CH), 4.02-3.56, 3.33(m, 4H, OCH_2 and pyrazoline CH_2), 2.17-0.74(m, 39H, other alkyl-H); ^{13}C NMR(50 MH$_Z$, $CDCl_3$), δ 163.5, 163.3, 155.9, 155.6, 153.1, 152.7, 151.8, 145.9, 142.8, 140.7, 140.3, 139.8, 139.3, 139.2, 138.7, 135.6, 133.6, 131.7, 131.3, 130.3, 128.7, 128.3, 127.1, 126.9, 126.0, 125.5, 121.5, 121.2, 120.6, 120.2, 119.9, 111.8, 111.5, 68.3, 68.0, 60.9, 60.4, 55.3, 55.1, 54.9, 43.3, 42.4, 40.3, 31.5, 31.4, 29.6, 29.3, 25.9, 23.8, 22.5, 13.9; IR(KBr pellet): 1602.5cm^{-1} (s,C=N).

3c: Yild:80%; ^{1}H NMR (400 MH$_Z$, $CDCl_3$), δ 7.89-6.88(m, 17H, ph-H), 6.33(m, 1H, pyrazoline CH), 4.04, 3.49(m, 4H, OCH_2 and pyrazoline CH_2), 2.22-0.75(m, 51H, other alkyl-H) ; ^{13}C NMR (50 MH$_Z$, $CDCl_3$); δ 163.5, 155.6, 153.1, 152.8, 151.9, 151.8, 151.9, 151.6, 143.0, 142.9, 140.7, 140.4, 139.8, 139.4, 139.2, 138.7, 133.7, 131.8, 130..3, 130.2, 128.9, 128.7, 128.3, 128.2, 127.2, 126.9, 126.0, 125.6, 125.3, 121.7, 121.6, 121.3, 120.7, 120.2, 119.9, 111.9, 111.5, 68.3, 68.1, 60.9, 55.3, 55.1, 42.4, 40.3, 31.9, 31.4, 29.7, 29.4, 29.3, 26.3, 23.8, 22.9, 22.5, 14.1, 13.9; IR (KBr pellet):1603.1cm^{-1}(s, C=N).

Results and Discussion

As shown in Scheme 1, monomer **1** and **2a-c** were easily polymerized to the corresponding polymers **3a-c** using palladium-catalyzed Suzuki coupling reaction. After the reaction was completed, the mixture was precipitated into a large amount of MeOH-H_2O(v:v, 10:1)system to obtain the crude polymer **3a-c** by filtration. Finally, purification using Soxhlet apparatus with acetone to remove the low molecular weight compounds, including catalyst residues, to give the corresponding polymers **3a-c** in moderate yields of 80-85% as a yellow powder. The results are summarized in table 1. Polymers **3a-c** had good solubility in common organic solvents such as THF, $CHCl_3$, CH_2Cl_2 and toluene. The polymers could be processed into transparent and uniform thin films by casting or spin-coating from toluene solution, and were found to be air stable in solution and in the solid state.

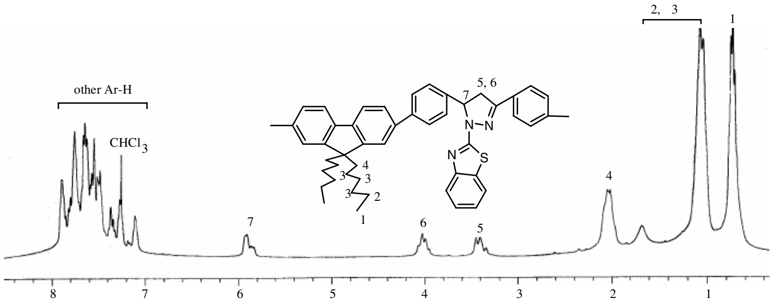
The molecular weight measurements were performed by gel permeation chromatography(GPC) in eluent THF using the calibration curve of polystyrene standards, as listed in stable 1. These copolymers have weight-average molecular weights (M_w) of 20900-34000 with polydisperity indices 1.71-2.02.

Table 1. Synthesis of the polymers **3a-c**[a]

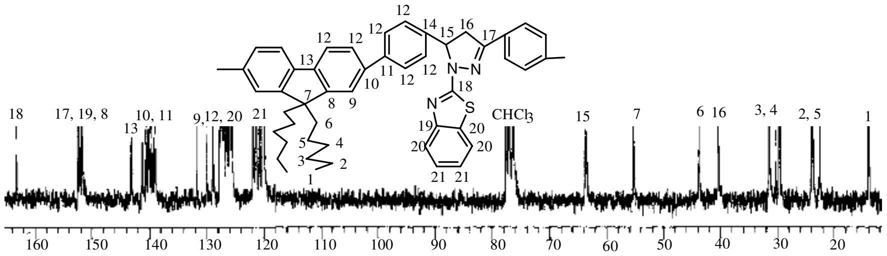
Polymer	Yield/%	M_w [b]	M_n [b]	M_w/M_n [b]	T_d[c]/°C	T_g[d]/°C
3a	84	28500	14100	2.02	412	210
3b	85	34000	17800	1.91	379	142
3c	80	20900	12200	1.71	387	120

[a]polymerization was carried out at 85-90 °C for 48 h under Ar. [b]GPC(THF), polystyrene standards. [c]TGA under N_2 [d]DSC under N_2

These polymers were characterized by their ^1H,^{13}C NMR and FT-IR. NMR spectra of polymer **3a** as a representative polymer were shown in Figure 1, In the ^1H NMR spectrum of **3a** in $CDCl_3$(Figure 1A), the signals of the alkyl chains dominated in the region of 0.72-2.1 ppm , and the pyrazoline unit appeared at 3.4-5.9 ppm. The signals of other aromatic protons were between 7.1 and 7.9 ppm. In the ^{13}C NMR spectrum of the polymer 3a (Figure 1B), typical signals of the benzothiazole unit carbons were dominant in the region of 121-164 ppm, and the pyrazoline moiety carbons appeared in the region of 40 to 156 ppm. The signals of alkyl carbons were between 13 to 64 ppm. The NMR spectra of polymers 3b-c were similar to polymer 3a and is not shown. The polymers 3a-c were also characterized by IR spectra, strong absorptions was observed at 1601.4, 1602.5 and 1603.1 cm^{-1}, respectively, which was characteristic of the carbon-nitrogen double bond. The thermal properties of the polymers were determined by TGA and DSC measurements. As shown in table 1 and figures 2-3. All these polymers show good thermal stability with the onset decomposition (Td) of 379-412 °C under nitrogen, and little weight loss was observed at lower temperature. After the temperature increaseing above 400 °C, the curves fall rapidly, indicating the decomposition of the polymer bacbones. The glass transition temperature (Tg) of the polymers range from 120 °C to 210 °C. These Tg values are much higher than those of poly(9, 9-dihexylfluorene)(PHF) and poly(9, 9-dioctylfluorene)(POF) (~51 °C), in which each repeating fluorene unit contain two flexible n-hexyl or n-octyl chain at C-9. It is obvious that the incorporation of benzothiazolylpyrazoline unit into the main chain can increase Tg of polyfluorenes. This is very important for such types of polymers used as emissive materials in PLEDs. [34]



(A) ^{1}H NMR spectrum of **3a**



(B) ^{13}C NMR spectrum of **3a**

Figure 1. NMR spectrum of polymer **3a** in $CDCl_3$

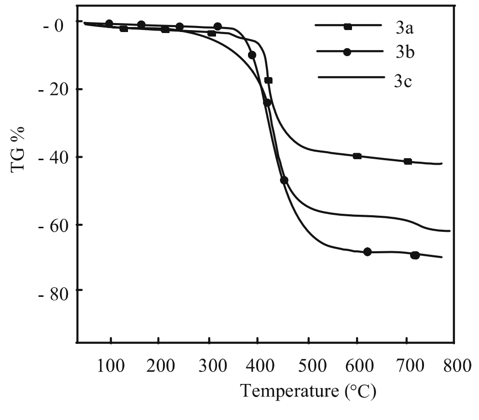


Figure 2. Thermal gravimetric analysis (TGA)curves of the polymers under nitrogen (10 °C/min)

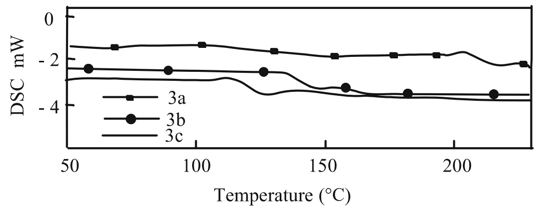


Figure 3. Differential scanning calorimetry(DSC)curves of the polymers under nitrogen (10°C/min)

The optical properties of the polymer **3a-c** are summarized in Table 2. The absorption and emission spectra of **3a-c** were shown in Figures 4-6, respectively.

Table 2. Optical properties of the polymers **3a-c**

	UV λ_{max}[a]/nm		PLλ_{max}[a,b]/nm		
polymer	solution	film	solution	film	Φ_{PL}[c]
3a	378	380	470	501	87
3b	374	382	468	530	82
3c	380	384	471	533	78

[a] Absorption and emission spectra were record in dilute $CHCl_3$ solutions at room temperature [b] Excited at absorption maxima [c] PL efficiencies in $CHCl_3$ determined relative to quinine sulfate in H_2SO_4(0.1M)

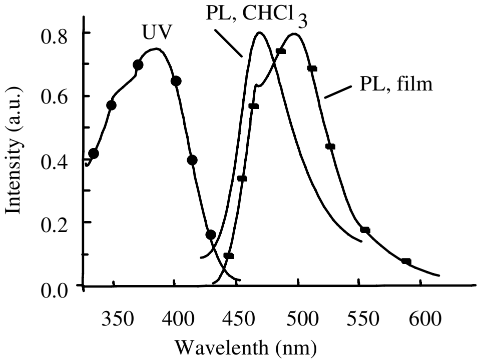


Figure 4. UV-vis absorption and photoluminescence spectra of **3a**

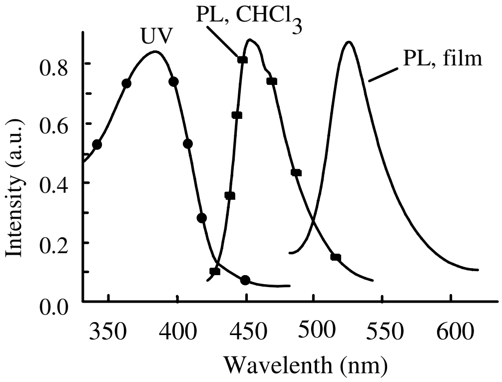


Figure 5. UV-vis absorption and photoluminescence spectra of **3b**

The absorption in solution was coincident with that in the solid state and is not shown. All polymers show very strong absorption peaks of 380 to 384 nm attributed to the π-π^* electronic transitions of the conjugated polymer backbones. A little red-shift appeared compare with PFs (absorption at 376 nm). In the fluorescence emission spectra of the polymers **3a-c** in dilute toluene solution at room temperature on

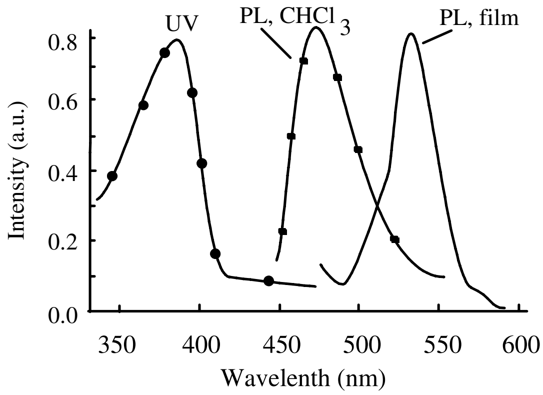


Figure 6. UV-vis absorption and photoluminescence spectra of **3c**

excitation at absorption maxima, the emission peaks were observed around 468-471 nm in the visible bluish-green region(Table 2, Figures 4-6). The polymer solutions exhibited 0.87, 0.82.and 0.78 quantum efficiency, respectively, as demonstrated by using quinine sulfate in 0.1M H_2SO_4 as standard(Φ=0.55). [35, 36] There are two reasons for the polymers show very strong photoluminescence. One is that small molecular pyrazolines themselves have excellent fluorescence. The other is the interchain interactions of the polymers were minishedd when bulky 1-(2-benzothiazol-yl)3, 5-diphenylpyrazolines unit with TICT structure was introduced into the main chain of PFs. In the thin solid films, the emission peaks appeared around 501-533 nm in the visible green region, (Table2, Figures 4-6). This red-shifted effect, very common in photoluminescent polymers, is usually due to the stronger interchain interactions that could significantly reduce the energy difference between LUMO and HOMO in solid states. And no typical emission from fluorene (at about 450 nm) was observed in the films, which implied that the emission of fluorene was quenched in these polymers., and the emission of the polymers come from the energy transfer from fluorene unit to pyrazoline unit.

Conclusion

Novel polymers with 1-(2-benzothiazolyl)-3,5-diphenylpyrazoline unit appended to the fluorene backbone were prepared by Suzuki coupling reaction. These polymers were soluble in common organic solvents, and transparent and uniform thin films of the polymers were obtained easily by casting or spin-coating form a toluene solution. All polymers' T_g values are much higher than that of typical polyfluorene, which reveals enough thermal stability of the titled polymers to be applied to electroluminescent materials. The polymers showed strong bluish-green photoluminescence in solution and green photoluminescence in the solid state. Further studies on the preparation of the 1-(2-benzothiazolyl)pyrazoline-containing polymers and their application as the light-emitting materials are now in progress.

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