

Synthesis and characterization of new fluorene-acceptor alternating and random copolymers for light-emitting applications

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Abstract

A series of novel light-emitting copolymers consisted of 9,9-dihexylfluorene (**F**) and different acceptor segments, including quinoxaline (**Q**), 2,1,3-benzothiadiazole (**BT**) and thieno[3,4-*b*]-pyrazine (**TP**), were synthesized by the palladium-catalyzed Suzuki coupling reaction. Three fluorene-acceptor alternating copolymers (**PFQ**, **PFBT**, **PFTP**) and six **F-TP** (**PFTP0.5–PFTP35**) random copolymers were investigated and compared with the parent polyfluorene (**PF**). The experimental results suggest that the acceptor strength or content significantly affect the electronic and optoelectronic properties. The optical absorption maxima of the **PF**, **PFQ**, **PFBT**, and **PFTP** are 368, 416, 470, and 578 nm, respectively, which indicates the significance of intramolecular charge transfer. The electrochemical band gap also shows a similar trend. The incorporation of the acceptor into the **PF** lowers the LUMO level and thus could improve the electron-accepting ability of the **PF**. The emission maxima on the photoluminescence (PL) spectra of the **PF**, **PFQ**, **PFBT**, and **PFTP** films are 424, 493, 540, and 674 nm, which correspond to the color of blue, green, yellow, and red, respectively. It suggests that the full color of emission can be achieved by different acceptors. The significant positive solvatochromism on the PL spectra in different polar solvents suggests the efficient intramolecular charge transfer in **PFTP**. However, such charge transfer or heavy-atom effect results in fluorescence quenching and thus reduces the PL efficiencies. By random copolymerizing the **TP** into the **PF**, the PL efficiency could be improved. A significantly reduction on the **PF** emission peak with increasing the **TP** content suggests the energy transfer between the **PF** and **TP** segments. Besides, the characteristics on the electroluminescence (EL) devices of ITO/PEDOT:PSS/emissive layer/Ca/Ag suggest that such energy transfer results in the complete quenching of the **PF** emission at only 1% **TP** content in the **PFTP01**. The maximum external quantum efficiency (EQE) of the EL device based on the **PFTP01** is superior to that of the **PF** due to the reduced LUMO level in matching with the Ca. The CIE 1931 coordinates of the **PFTP01** based EL device under the condition of maximum EQE is (0.66, 0.31), which is close to the standard red of (0.66, 0.34) demanded by the National Television System Committee (NTSC). The luminescence characteristics based on the prepared polymers depend on the Förster energy transfer or the intramolecular charge transfer, or heavy-atom fluorescence quenching. The present study suggests that the tuning of the electronic and optoelectronic properties could be achieved by incorporating various acceptors or content into the polyfluorenes.

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Keywords: Polyfluorene; Charge transfer; Luminescence

1. Introduction

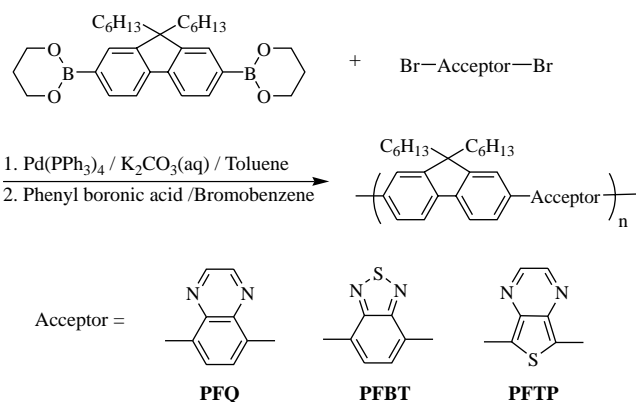
Conjugated polymers have been extensively studied for their potential applications in electroluminescence displays [1,2], photovoltaic devices [3,4], and thin film transistors [5–7]. They not only combine the physical properties of polymers with those of semiconductors to obtain unique and novel

materials but also provide tunable electronic and/or mechanical properties by structure modification [8]. The band structures of conjugated polymers can be manipulated by minimization of bond length alternation [9,10] and incorporation of donor–acceptor units [11,12], which are key to tune their electronic and optoelectronic properties. We are particularly interested in the donor–acceptor alternating copolymers since their electronic properties are tuned efficiently by intramolecular charge transfer (ICT) [11–14].

Polyfluorenes (**PFs**) have been widely studied for polymer light-emitting diodes (PLED) because of their processibility, high quantum yield, and good charge transport properties [15]. However, the poor electron-transporting property of polyfluorene results in a large electron-injection barrier and unbalance

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Scheme 1. Synthesis of the fluorene-acceptor alternating copolymers, **PFQ**, **PFBT**, and **PFTP**.

of charge carrier transport for the PLED application. Therefore, copolymerization of fluorene with various electron-accepting and/or electron-transporting moieties has been investigated to improve this shortcoming [16]. Recently, donor-acceptor conjugated copolymers based on fluorene with various acceptors were reported in the literature, including benzothiadiazole [16], pyridine [17], bithiazole [18], naphthoselenadiazole [19], indenofluorene [20], quinoxaline [21], and perylene [22]. The light-emitting color or efficiency of PLED based on the fluorene-acceptor copolymers were easily tuned by the acceptors. Besides, photovoltaic devices with good efficiencies were demonstrated by poly(9,9-dioctylfluorene-*alt*-benzothiadiazole) (F8BT) [23]. High electron mobility from the F8BT-based field effect transistor was also reported recently [24].

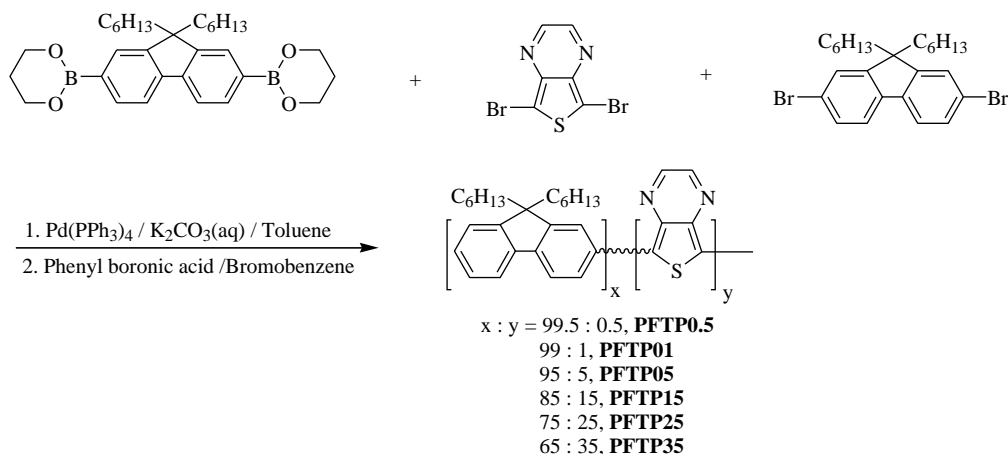
Although various fluorene based donor-acceptor copolymers have shown tunable optoelectronic properties and promising device applications, the effects of the acceptor strength on the optoelectronic properties have not been addressed yet. In this study, three fluorene-acceptor alternating and six random conjugated copolymers were synthesized using palladium(0)-catalyzed Suzuki coupling reaction and compared, as shown in Schemes 1 and 2, respectively. The physical properties of the synthesized donor-acceptor conjugated polymers were compared with those of the parent

poly[2,7-(9,9-dihexylfluorene)] (**PF**). The studied acceptors included quinoxaline (**Q**), 2,1,3-benzothiadiazole (**BT**) and thieno[3,4-**b**]pyrazine (**TP**). The LUMO of the **Q**, **BT**, and **TP** are -0.90 , -1.81 , and -1.41 eV, respectively [25], which indicates the order of the acceptor strength is **BT** > **TP** > **Q**. Thus, the effects of acceptor strength and intramolecular charge transfer between fluorene and acceptor segments on the optoelectronic properties can be explored. Besides, six fluorene-**TP** random copolymers were synthesized for investigating the effects of the **TP** content on the optoelectronic properties. The feeding ratios of the 9,9-dihexylfluorene-2,7-bis(trimethylborate) and 9,9-dihexyl-2,7-dibromofluorene to the **TP** are 99.5:0.5, 99:1, 95:5, 85:15, 75:25, and 65:35 for the random copolymers of **PFTP0.5**, **PFTP01**, **PFTP05**, **PFTP15**, **PFTP25**, and **PFTP35**, respectively. Electroluminescence (EL) devices fabricated from the synthesized polymers as emissive layers were characterized. The possible energy transfer from the fluorene to fluorene-acceptor segment was investigated. The color tuning ability of the EL devices through various acceptors or content was also demonstrated in this study.

2. Experimental

2.1. Materials

2,1,3-Benzothiadiazole, bromine, glacial acetic acid, zinc dust, glyoxal (40 wt% in water), 3,4-diaminothiophene dihydrochloride, *N*-bromosuccinimide, 9,9-dihexylfluorene-2,7-bis(trimethylborate), 9,9-dihexyl-2,7-dibromofluorene, tetrakis(triphenylphosphine)-palladium(0), potassium carbonate, and trioctylmethylammonium chloride (aliquat[®] 336), were purchased from Aldrich (Missouri, USA) or Acros (Geel, Belgium) and used without further purification. Ultra-anhydrous solvents used in the reactions were purchased from Tedia (Ohio, USA). The following acceptor monomers were prepared according to literature procedures: 4,7-dibromo-2,1,3-benzothiadiazole [26], 5,8-dibromoquinoxaline [27,28], and 5,7-dibromothieno[3,4-*b*]pyrazine [29,30].



Scheme 2. Synthesis of the fluorene-**TP** copolymers, **PFTP0.5**–**PFTP35**.

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