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Synthesis and luminescent properties of block copolymers based on polyfluorene and polytriphenylamine

Ying Tan, Zhijie Gu, Kousuke Tsuchiya, Kenji Ogino*

Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, 2-24-16 Nakacho, Koganei-shi, Tokyo 184-8588, Japan

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ABSTRACT

For the preparation of block copolymers containing polyfluorene (PF) and hole transporting segment, PF homopolymers with diphenylamine terminals were synthesized by Suzuki coupling polymerization. The terminals of PF were converted to polytriphenylamine (PTPA) block by C–N coupling polymerization to give PTPA-*block*-PF-*block*-PTPA (PF-PTPA) triblock copolymers with different PTPA chain lengths. These polymers were soluble in common organic solvents and readily formed thin films by solution processing. All of the polymers exhibited similar UV absorption and PL emission properties both in chloroform solution and in film state. PF-PTPA block copolymers showed relatively high HOMO compared with that of PF by cyclic voltammetry. Compared with corresponding PF homopolymers, the EL devices based on PF-PTPA block copolymers showed higher luminance and current efficiency than those of PF homopolymers because of the improvement of hole injection by the introduction of PTPA segment.

1. Introduction

Polyfluorenes (PFs), which possess a relatively large band gap, have been widely investigated as a blue PLED material because of their superior properties, such as highly efficient photoluminescence (PL), excellent thermal stability, and good solubility in common organic solvents [1,2]. However, they exhibit insufficient color stability causing troublesome long wavelength emission band (520–560 nm), assigned to aggregates/excimers, interchain interactions, and/or an emissive keto defect generated by thermo-, photo-, or electro-oxidative degradation during device operation [3–6]. In fact, various kinds of modifications were proposed to prepare polyfluorene-based copolymers to improve the performance. For example, an alkyl/phenyl structure was introduced at the C-9 position to reduce the aggregation and keto defect [7–10], or end-capping groups were attached to PF backbones to suppress the green emission by keeping the recombination zone away from the polymer/anode interface and by increasing the hole-trap efficiency [11]. Another serious problem associated with PF is poor electroluminescence (EL) efficiency due to an imbalance in charge carriers caused by large hole injection barriers and different charge carrier mobilities [12]. Therefore, PFs require additional hole-transporting layers to obtain efficient hole injection/transport in EL device.

Triphenylmaine (TPA) derivatives have been known as candidates for hole transporting materials to be used in organic EL and photovoltaic cell devices. Many compounds containing the TPA moiety for EL devices have been reported for decades [13–16]. Furthermore, some researchers employed triphenylamine as a polymer backbone for building up the π-conjugated structure of poly(triphenylamine) (PTPA) [17–20] because PTPA has been found to a) facilitate hole injection and transport from the anode and b) serve as an electron-blocking layer, which blocks electron movement to the anode and confines excitons within the emission layer to reduce green emission [5,6]. Previously, we reported that PTPA can be synthesized via C–N coupling polymerization of a self-condensing monomer by palladium catalyst [21]. This technique allows us to assemble PTPA into the block copolymer architectures by the chain elongation from terminals of the other polymer.

Incorporating some functional components such as charge transport and luminescent moieties into a copolymer can easily adjust the balance between hole and electron injections in the emitting layer in polymer EL devices. For example, multilayer blue-emitting EL device based on fluorene-triarylamine alternating copolymer with a high hole mobility showed a high current efficiency as 8.7 cd/A [22]. Moreover, we demonstrated that the device based on bipolar charge transporting block copolymers showed higher external quantum efficiency compared with random copolymers or polymer blends with the same composition [23,24]. The microphase-separated structure built in the block copolymer layer afforded the effective charge recombination [25,26]. The block

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* Corresponding author. Tel./fax: +81 42 388 7404.
E-mail address: kogino@cc.tuat.ac.jp (K. Ogino).

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copolymer containing polyfluorene segment was also reported by the other authors [27]. In this work, block copolymers consisting of PF and PTPA were synthesized for a luminescent material in EL devices. PTPA segments were introduced at the terminals of PF for improvement of hole injection/transport at the PF layer. In order to convert the terminals of PF to diphenylamine group, polymerization method of the fluorene monomer(s) was optimized. The terminal-modified PFs were sequentially altered to the block copolymers by C–N coupling polymerization. The structures of PF homopolymers and block copolymers were characterized by GPC and ^{1}H NMR. The photophysical and electrical properties of the polymers as well as performance of the EL device based on them were examined.

2. Experimental

2.1. Materials

All reagents and solvents were used without further purification unless stated otherwise. Tetrahydrofuran (THF) was distilled over sodium and benzophenone, and stored under nitrogen atmosphere. Toluene was distilled over calcium hydride, and stored under nitrogen atmosphere. The other reagents and solvents were obtained commercially and were used as received.

2.2. Synthesis of 2,7-dibromofluorene (*1*)

Fluorene (16.62 g, 0.10 mol), 2,6-*t*-butyl-4-cresol (0.04 g, 0.182 mmol), $FeCl_3$ (0.4010 g, 2.48 mmol), and chloroform (300 mL) were added into a flask under nitrogen atmosphere and cooled down to −78 °C, and then bromine (12.5 mL, 0.244 mmol) was added dropwise slowly. After reaction for 24 h at r.t., $NaHSO_3$ aq. (300 mL) was added. The product was extracted with chloroform and dichloromethane, and the organic layer was dried with $MgSO_4$. After the organic layer was concentrated by rotary evaporator, the crude product was recrystallized from methanol once or twice. White crystal (26.64 g in total) was obtained. The yield was 82%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.68 (s, 2H, ArH), 7.60 (d, $J = 9.0$ Hz, 2H, ArH), 7.52 (d, $J = 9.0$ Hz, 2H, ArH), 3.87 (s, 2H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 144.87, 139.78, 130.24, 128.40, 121.30, 121.02, 36.65. HR-MS (*m/z*): calcd for $C_{13}H_8Br_2$, 321.8993; found, 323.8999 $[M]^+$.

2.3. Synthesis of 2,7-dibromofluoren-9-one (*2*)

To a flask equipped with a stopcock were added **1** (20.0 g, 61.7 mmol) and acetic acid (150 mL) under nitrogen atmosphere. A solution of CrO_3 (15 g, 150 mmol) dissolved in acetic acid (120 mL) was added. After reaction for 24 h at r.t., the solution was neutralized with sodium bicarbonate aq. and the precipitate was filtrated. The crude product was recrystallized from ethanol and chloroform twice. Yellow crystal (10.02 g in total) was obtained. The yield was 48%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.72 (d, $J = 3.0$ Hz, 2H, ArH), 7.60 (dd, $J = 6.0$ Hz, 2H, ArH), 7.35 (d, $J = 9.0$ Hz, 2H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 191.01, 142.28, 137.57, 135.30, 127.88, 123.42, 121.96. HR-MS (*m/z*): calcd for $C_{13}H_7Br_2O$, 336.8864; found, 336.8864 $[M + H]^+$.

2.4. Synthesis of 2,7-dibromo-9-(4-octylphenyl)fluoren-9-ol (*3*)

To a 100-mL flask equipped with a stopcock and a condenser were placed Mg (0.28 g, 12.0 mmol), 1,2-dibromoethane (0.020 mL, 0.23 mmol), and THF (2.0 mL) under nitrogen atmosphere. When Mg began to react, a solution of 4-bromooctylbenzene (3.0 g, 11 mmol) dissolved in THF (2.0 mL) was added, and the mixture was refluxed until Mg reacted completely. The solution was cooled down to r.t., THF (37 mL) and **2** (2.80 g, 8.3 mmol) were added and the mixture was refluxed for 16 h. After reaction for 2 h at r.t., the mixture was treated with saturated NH_4Cl aq., extracted with diethyl ether. The organic layer was washed with brine, dried with $MgSO_4$, and concentrated by rotary evaporator. The crude product was purified by column chromatography (chloroform:hexane = 1:1). White solid was obtained. The yield was 2.35 g (54%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.49 (s, 4H, ArH), 7.45 (s, 2H, ArH), 7.25 (d, $J = 6.0$ Hz, 2H, ArH), 7.11 (d, $J = 6.0$ Hz, 2H, ArH), 2.56 (t, $J = 6.0$ Hz, 2H, CH_2), 2.49 (s, 1H, −OH), 1.58 (m, 2H, CH_2), 1.27 (m, 10H, CH_2), 0.87 (t, $J = 6.0$ Hz, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 152.26, 142.70, 138.93, 137.57, 132.42, 128.64, 128.42, 125.23, 122.58, 121.61, 83.37, 35.74, 32.00, 31.51, 29.58, 29.54, 29.37, 22.80, 14.26. HR-MS (*m/z*): calcd for $C_{27}H_{28}Br_2O$, 526.0507; found, 526.0549 $[M]^+$.

2.5. Synthesis of 2,7-dibromo-9-(4-methylphenyl)-9-(4-octylphenyl) fluorene (*4*)

To a flask equipped with a stopcock were placed **3** (2.00 g, 3.92 mmol) and distilled toluene (48 mL) under nitrogen atmosphere, heated up to 60 °C. After trifluoromethanesulfonic acid (0.68 mL, 7.75 mmol) was added, the mixture was stirred for 2 h. The solution was neutralized with sodium bicarbonate aq. and extracted with ethyl acetate, and the organic layer was dried with $MgSO_4$. After ethyl acetate was removed by rotary evaporator, the crude product was purified by column chromatography (hexane:ethyl acetate = 30:1). White solid was obtained. The yield was 1.91 g (83%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.57 (d, $J = 6.0$ Hz, 2H, ArH), 7.48 (d, $J = 3.0$ Hz, 2H, ArH), 7.46 (s, 2H, ArH), 7.04 (m, $J = 3.0$ Hz, 8H, ArH), 2.55 (t, $J = 6.0$ Hz, 2H, CH_2), 2.31 (s, 3H, CH_3), 1.55 (m, 2H, CH_2), 1.27 (m, 10H, CH_2), 0.87 (t, $J = 6.0$ Hz, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 153.53, 141.98, 141.74, 141.69, 138.13, 136.90, 130.91, 129.51, 129.33, 128.61, 128.00, 127.95, 121.92, 121.63, 65.18, 35.65, 32.04, 31.50, 29.60, 29.38, 22.82, 21.12, 14.27. HR-MS (*m/z*): calcd for $C_{34}H_{34}Br_2$, 600.1027; found, 600.1088 $[M]^+$.

2.6. Synthesis of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9- (4-methylphenyl)-9-(4-octylphenyl)fluorene (*5*)

A solution of **4** (0.903 g, 1.5 mmol) dissolved in 10 mL of THF was added to a flask equipped with a stopcock under nitrogen atmosphere, and cooled to −78 °C. Then, *n*-butyllithium (1.34 mL, 2.6 M solution in hexane) was added dropwise, and the mixture was stirred for 30 min. To this mixture, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.674 g, 9.0 mmol) was added, and the mixture was stirred for 12 h. The reaction mixture was quenched with brine, and extracted with diethyl ether. The organic layer was washed with brine, dried with $MgSO_4$, and concentrated by rotary evaporator. The crude product was purified by column chromatography on silica gel with hexane:ethyl acetate = 10:1 as an eluent. White solid was obtained. The yield was 0.41 g (39%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.81 (d, $J = 6.0$ Hz, 4H, ArH), 7.77 (d, $J = 6.0$ Hz, 2H, ArH), 7.11 (dd, $J = 3.0$ Hz, 4H, ArH), 7.01 (dd, $J = 3.0$ Hz, 4H, ArH), 2.25 (s, 3H, CH_3), 1.55 (m, 2H, CH_2), 1.31 (m, 24H, CH_3), 1.28 (m, 10H, CH_2), 0.87 (m, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 151.63, 143.03, 142.96, 142.90, 141.09, 135.99, 134.26, 132.47, 128.95, 128.48, 128.40, 128.23, 119.90, 119.89, 83.80, 65.01, 35.67, 32.06, 31.53, 29.62, 29.43, 25.05, 25.03, 22.81, 21.11, 14.28. Anal. Calcd for $C_{46}H_{58}B_2O_4$: C, 78.24, H, 7.08; Found: C, 78.07, H, 6.80.

2.7. Synthesis of 1-{2-(2-(2-methoxyethoxy)ethoxy)ethoxy}-4-nitrobenzene (*6*)

To a flask equipped with a Dean–Stark apparatus were placed triethylene glycol monomethyl ether (16.32 g, 0.1 mol), potassium