



Synthesis of dual-emissive polymers based on ineffective energy transfer through cardo fluorene-containing conjugated polymers



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ABSTRACT

We describe here the design and synthesis of the conjugated polymers containing dye-modified cardo fluorenes for the dual emissions. Mono and di-substituted cardo fluorenes with boron dipyrromethene (BODIPY) were introduced into alternating conjugated polymers using bis-thienyl-benzothiadiazole as a comonomer for constructing the donor (D)-acceptor (A) pairs through the main-chains. The polymeric products showed good solubility in the common organic solvents and good film-formability. Strong emissions were obtained from the synthesized polymers in both solution and film states. In particular, multi-color emissions in green and red regions derived from each component were observed from the solutions containing the synthesized polymers. From the emission lifetime measurements, it was found that the energy transfer should be suppressed between the side and the main-chains, leading to the dual emission from the polymers. Furthermore, we also observed that the synthesized polymers have the light-harvesting antenna (LHA) effects and the color tunability by changing the number of BODIPY dyes tethered to the cardo fluorene.

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1. Introduction

Dual-emissive polymers which show the two kinds of emissions from a single material in the different wavelength regions with the excitation at the single wavelength light are versatile not only for preparing optical devices but also for applying to the bio-sensors [1]. For instance, the white light-emissive materials which are applicable as an artificial illumination or a back light in the display were manufactured from the combination with the red, green, and blue chromophores [1]. By introducing these dyes into the polymers with or without covalent bonds, the multiple emission can be obtained, leading to the white-light emission for the human eyes. The emission colors were also tuned by the composition ratio. Dual emissions originated from the radiative transitions from the different excited states such as locally excited and charge transfer (CT) states [2] or singlet and triplet excited states [3] were used as the sensing technology for the biomolecules. By comparing the intensities of each emission band, the detection was achieved for the base-pairing in DNA [2] and oxygen concentration [3]. To observe such dual emissions, the transitions from different excited

states are essential with the suppression of the energy transferring between these energy states. However, it is often the case with the dyads, by connecting two kinds of fluorescent dyes closely, the energy transferring proceeds efficiently even though the overlapping of the spectra of the donor and the acceptor is very small, resulting in the single emission. Therefore, the elaboration on the molecular design for receiving each emission individually is necessary to obtain the dual emission with high efficiency.

We have reported the isolation effect from the electronic interaction by the cardo structure in polyfluorenes [4]. It was shown that the influence of the electron-withdrawing and donating groups tethered to the polyfluorene via the cardo carbons can be completely inhibited. Therefore, the pure blue emissions were observed from a series of the modified polyfluorenes with various electron-positive and negative units. In addition, it was also presented that by tethering the fluorophores to polyfluorene via the cardo carbon, the concentration quenching can be avoided [5]. Therefore, there is large possibility to realize the multi-functional emissive polymers based on the preprogrammed design without loss of intrinsic optical properties of the components by undesired energy transfer or electronic interaction. Thus, we proposed that the cardo fluorene should be a versatile nanobuilding block for assembling the optically-functional molecules without loss of their functions. On the other hand, it is still unchallenged to control the

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energy transfer efficiency between the side chains and the polymer main-chains. Next goal is to establish the suppression of energy transferring with the side chains and receive the emissions individually from each component. In particular, we aim to realize the multi-emission based on the cardo structure-containing modified polyfluorene with emissive dyes by inhibiting the energy transfer between main and side chains.

Herein, we present the dual-emissive polymers involving the cardo fluorene structure. To suppress the energy transfer between the chromophore and the polymer, we employed the boron dipyrromethene (BODIPY) dye and the conjugated polymer composed of the D-A alternative structure because of the small overlapping of their emission and absorption spectra, respectively. A series of the modified cardo fluorene with single and dual BODIPY molecules were conjugated with a bis-thienyl-benzothiadiazole-containing acceptor unit, and the optical properties were evaluated. BODIPYs are well known as a versatile fluorophore in material science as well as biotechnology. However, it is often observed that optical properties of BODIPYs were critically spoiled by agglomeration because of the strong aggregation ability. In addition, most of the BODIPY-containing polymers also showed the loss of optical properties via the concentration quenching. In contrast, we observed the dual emissions in green and red regions originated from the BODIPY units and the D-A-type conjugated polymer moieties, respectively. Furthermore, we observed the synthesized polymers can possess the LHA effect and the color tenability by modulating the number of the substituted dyes via the cardo fluorene. Rational design for receiving multi-color emission from the single material is demonstrated.

2. Experimental section

2.1. General

^1H , ^{13}C and ^{11}B NMR spectra were measured with a JEOL EX-400 (400 MHz for ^1H , 100 MHz for ^{13}C , 128 MHz for ^{11}B) spectrometer. Coupling constants (J value) are reported in Hertz. ^1H and ^{13}C NMR spectra used tetramethylsilane (TMS) as an internal standard. ^{11}B NMR spectra were referenced externally to $\text{BF}_3\cdot\text{OEt}_2$ (sealed capillary) in CDCl_3 . The number-average molecular weight (M_n) and the molecular weight distribution [weight-average molecular weight/number-average molecular weight (M_w/M_n)] values of all polymers were estimated by size-exclusion chromatography (SEC) with a TOSOH G3000HXL system equipped with three consecutive polystyrene gel columns [TOSOH gels: α -4000, α -3000, and α -2500] and ultraviolet detector at 40 °C. The system was operated at a flow rate of 1.0 mL/min, with CHCl_3 as an eluent. Polystyrene standards were employed for calibration. UV–vis spectra were recorded on a Shimadzu UV-3600 spectrophotometer. Fluorescence emission spectra were recorded on a HORIBA JOBIN YVON Fluoromax-4 spectrofluorometer, and the absolute quantum yield was calculated by integrating sphere method on the HORIBA JOBIN YVON Fluoromax-4 spectrofluorometer in chloroform. Fluorescence lifetime analysis was carried out on a HORIBA FluoreCube spectrofluorometer system; excitation at 375 nm was carried out using a UV diode laser (NanoLED-375L).

2.2. Materials

Tetrahydrofuran (THF), diethyl ether (Et_2O), and triethylamine (Et_3N) were purified using a two-column solid-state purification system (Glasscontour System, Joerg Meyer, Irvine, CA). 2,7-Dibromo-9,9-didodecylfluorene was obtained commercially, and used without further purification. 4,7-Bis-(3-hexylthiophen-2-yl)benzo[1,2,5]thiadiazole, monomers **1** and **2** were prepared

according to the literature [5]. All reaction was performed under argon atmosphere.

2.3. 4,7-Bis[4-hexyl-5-(trimethylstannyl)thiophen-2-yl]benzo[1,2,5]thiadiazole (**3**)

A THF solution of 2,2,6,6-tetramethylpiperidine (TMP) (1.5 mL, 8.8 mmol) was cooled to -78 °C and, *n*-butyllithium in hexane (5.0 mL, 8.0 mmol, 1.6 M) was added. After the solution was allowed to warm until room temperature in 20 min, the resulting solution was cooled to -78 °C, again. A solution of 4,7-bis-(3-hexylthiophen-2-yl)benzo[1,2,5]thiadiazole (1.62 g, 3.46 mmol) in THF (10 mL) was added and stirred for 30 min. Then, 1 M solution of trimethyltin chloride in hexane was added, and the reaction mixture was allowed to warm to room temperature. After stirring for 20 h, water was added, followed by extraction with cyclopentyl methyl ether (CPME). The mixture was washed three times with 0.1 M hydrochloric acid to remove TMP. After drying over MgSO_4 and removal of the solvent under vacuum, compound **3** (2.70 g, 98%) was obtained as a yellow solid after recrystallization in ethanol twice. ^1H NMR (CDCl_3 , ppm) δ 7.60 (s, 2H), 7.16 (s, 2H), 2.67 (t, $J = 8.2$ Hz, 4H), 1.68–1.56 (m, 4H), 1.31–1.12 (m, 12H), 0.81 (t, $J = 6.5$ Hz, 6H), 0.41 (s, 18H). ^{13}C NMR (CDCl_3 , ppm) δ 154.27, 142.88, 138.47, 138.01, 137.53, 129.49, 127.58, 31.54, 30.82, 29.23, 22.51, 18.43, 14.01, -8.14 . HRMS (p-MALDI) Calcd for $\text{C}_{32}\text{H}_{48}\text{N}_2\text{S}_3\text{Sn}_2$: m/z 796.10181; Found: m/z 796.10580.

2.4. Synthesis of polymer **P1**

A typical polymerization protocol via the Stille coupling reaction is shown here: A solution containing monomer **1** (91 mg, 100 μmol), **3** (79 mg, 100 μmol), $\text{Pd}_2(\text{dba})_3$ (1 mg, 1 μmol) and tri(2-furyl)phosphine (2 mg, 9 μmol) in 1 mL of anhydrous toluene was stirred at 100 °C for 5 days under argon atmosphere. The resulting products were reprecipitated twice with a small amount of chloroform into 50 mL of methanol. Filtration gave a red solid (110 mg, 91%). ^1H NMR (CDCl_3 , ppm) δ 7.80 (2H), 7.71 (2H), 7.39 (4H), 7.51 (1H), 7.42 (2H), 7.34 (1H), 7.24 (2H), 7.19 (2H), 6.83 (2H), 3.93 (2H), 2.67 (4H), 2.50 (6H), 2.26 (4H), 1.76 (2H), 1.72 (4H), 1.42 (2H), 1.29 (20H), 1.21 (6H), 0.86 (15H). ^{13}C NMR (CDCl_3 , ppm) δ 158.27, 154.15, 153.61, 152.62, 146.96, 144.78, 142.99, 139.99, 139.24, 138.36, 134.33, 133.96, 132.61, 131.86, 130.78, 129.69, 129.18, 128.77, 128.38, 127.25, 125.70, 125.53, 123.27, 120.73, 114.54, 68.03, 64.94, 31.79, 31.55, 30.72, 29.65, 29.33, 29.28, 26.06, 22.63, 22.54, 17.07, 14.57, 14.06, 14.02, 12.44, 11.79, 11.72. ^{11}B NMR (CDCl_3 , ppm) δ 0.77.

2.5. Synthesis of polymer **P2**

Similarly to the preparation of **P1**, polymer **P2** was prepared from **2** (59 mg, 70 μmol) and **3** (43 mg, 70 μmol) in the presence of $\text{Pd}_2(\text{dba})_3$ (0.5 mg, 0.6 μmol) and tri(2-furyl)phosphine (1.0 mg, 4 μmol) in 92% yield as a red solid (70 mg). ^1H NMR (CDCl_3 , ppm) δ 7.84 (2H), 7.75 (2H), 7.65 (4H), 7.56 (2H), 7.44 (4H), 7.36 (2H), 7.23 (2H), 2.67 (4H), 2.50 (12H), 2.26 (8H), 1.65 (4H), 1.32 (12H), 1.12 (12H), 0.91 (12H), 0.81 (6H). ^{13}C NMR (CDCl_3 , ppm) δ 154.13, 153.76, 152.17, 145.95, 145.48, 144.67, 143.08, 139.63, 139.30, 138.26, 134.97, 134.77, 134.18, 132.88, 132.81, 131.96, 130.72, 129.74, 128.64, 128.58, 127.26, 126.06, 125.74, 125.60, 123.17, 120.90, 65.53, 31.52, 30.72, 29.62, 29.13, 22.52, 17.06, 14.57, 14.00, 12.43, 11.86. ^{11}B NMR (CDCl_3 , ppm) δ 0.78.

2.6. Synthesis of polymer **P3**

Similarly to the preparation of **P1**, polymer **P3** was prepared from 2,7-dibromo-9,9-didodecylfluorene (66 mg, 100 μmol) and **3**

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