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Highly Efficient Circularly Polarized Light Emission in the Green Region from Chiral Polyfluorene–Thiophene Thin Films

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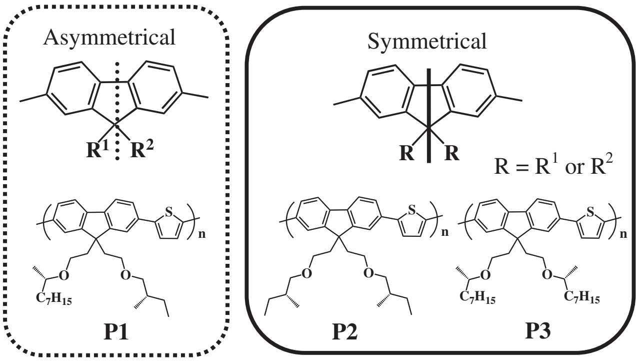
A chiral polyfluorene–thiophene derivative incorporating two different chiral side chains was synthesized via the Suzuki coupling reaction. Upon photoexcitation, thin films of the polymer exhibited efficient circularly polarized luminescence in the visible range, even without thermal annealing. The dissymmetry factor, g_{lum}, of films with thicknesses less than 100 nm reached 0.2 at 505 nm.

Chiral conjugated polymers have attracted considerable attention because of their interesting chiroptical properties such as circular dichroism (CD) and circularly polarized luminescence (CPL) in the visible region.[1,2] Because of these properties, these polymers have potential applications in organic chiropto-electronic, circularly polarized electroluminescence (CPEL) and circularly polarized photodiode (CPPD) devices.[3,4] In particular, polyfluorene and polythiophene derivatives incorporating chiral side chains exhibit relatively clear CD signals and have been studied for quantitative interpretation of chiroptical properties.[5,6] One of the major goals in this field is to improve the dissymmetry factors for absorption (g_{abs}) and luminescence (g_{lum}) introduced by Kuhn.[7] These factors are respectively defined as $g_{\mathrm{abs}} = 2(A_{\mathrm{L}} - A_{\mathrm{R}})/(A_{\mathrm{L}} + A_{\mathrm{R}})$ (A_{L} and A_{R}: absorbance for left and right circularly polarized lights, respectively) and $g_{\mathrm{lum}} = 2(I_{\mathrm{L}} - I_{\mathrm{R}})/(I_{\mathrm{L}} + I_{\mathrm{R}})$ (I_{L} and I_{R}: luminescence intensity of left and right circularly polarized lights, respectively). This means that larger ($A_{\mathrm{L}} - A_{\mathrm{R}}$) and ($I_{\mathrm{L}} - I_{\mathrm{R}}$) values are required to achieve higher g_{abs} and g_{lum} values. For achieving high ($A_{\mathrm{L}} - A_{\mathrm{R}}$) and ($I_{\mathrm{L}} - I_{\mathrm{R}}$) values, the formation of higher-order structures of chiral polymers has attracted considerable attention.[8,9]

One of the most interesting studies on π-conjugated systems is on the chiropto-electronic applications of chiral fluorene oligomers by Geng et al.[10] They obtained a value of 0.35 for the dissymmetry factor of electroluminescence (g_{CPEL}) for a 100-nm-thick film. Till date, this is the highest reported value in the blue region. There have been no reports of materials exhibiting g_{abs}, g_{lum}, and g_{CPEL} values above 0.1 in the green and red regions, except for materials asymmetrically amplified by external stimuli such as thermal annealing.[11,12] It seems that the formation of higher-order chiral structures with efficient electroluminescence in the long-wavelength (over 500 nm) regions is difficult.

To improve the chiroptical properties in the green region, we have focused on chiral polyfluorene–thiophene derivatives because the polyfluorene–thiophene backbone is well known for its remarkable absorption and luminescence properties in the green region.[13] We previously reported that chiral polyfluorene–thiophene derivatives exhibited large CD signals around the green region in a mixed chloroform/methanol solution.[14] However, 100-nm-thick films of these polymers exhibited only a small CD signal.



Scheme 1. Structures of chiral polyfluorene–thiophene copolymers composed of asymmetric (**P1**) and symmetric (**P2** and **P3**) fluorene units.

Herein, we present the first report of novel chiral polyfluorene–thiophene derivatives that exhibit highly efficient CD and CPL signals in the green region. A series of polyfluorene–thiophene derivatives incorporating chiral side chains, **P1**, **P2**, and **P3**, were synthesized, as shown in Scheme 1.[25] To change their aggregation properties, two different side chains were introduced at the 9 position of the fluorene unit to afford **P1**. It is assumed that the asymmetric structure of the fluorene unit leads to a slower aggregation process, which is advantageous for efficient chiral packing. These polymers were synthesized via the Suzuki coupling reaction by using chiral dibromofluorene monomers and thiophene 2,5-diboronic methyl ester (yield: 50–70%). The number-average molecular weights (M_{n}) of **P1**, **P2**, and **P3** were 9100, 6500, and 8800, respectively, and their weight-average molecular weights (M_{w}) were 13700, 12200, and 13000, respectively. The degrees of polymerization of **P1**, **P2**, and **P3** were 17, 14, and 15, respectively. The obtained polymers were soluble in common organic solvents such as chloroform and tetrahydrofuran and insoluble in hexane and methanol.

The optical and chiroptical properties of the polymer thin films were evaluated using ultraviolet–visible (UV–vis) absorption and CD and CPL measurements. Figure 1 shows the UV–vis absorption and corresponding CD spectra for 80-nm-thick spin-coated films of (a) **P1**, and (b) **P2** and **P3** prepared from chloroform solutions on quartz substrates. All the films prepared in this study were sufficiently transparent for optical measurements. **P1**, **P2**, and **P3** exhibited maximum absorption peaks at 439, 467 (**P1**), 434 (**P2**), and 434 nm (**P3**), resulting from π–π* transitions. Spin-coated **P2** and **P3** films showed a relatively small Cotton effect in the π–π* region. Moreover, the chirality

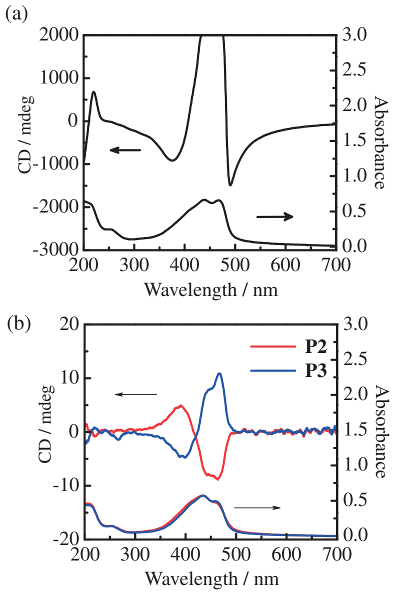


Figure 1. CD and UV–vis absorption spectra of spin-coated chiral polyfluorene-thiophene films (80 nm thick) prepared from 10 mg mL^{-1} chloroform solutions: (a) **P1**, and (b) **P2** and **P3**.

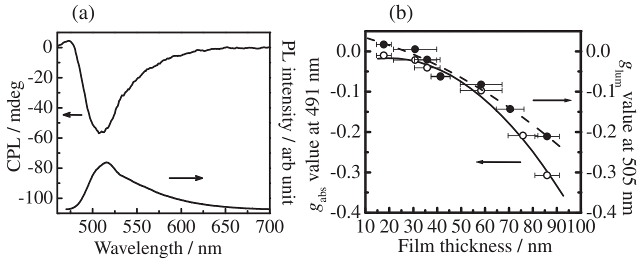


Figure 2. (a) CPL (λ_{ex} 380 nm) and PL (λ_{ex} 465 nm) spectra of an 80-nm-thick **P1** spin-coated film. (b) g_{abs} and g_{lum} values at 491 and 505 nm, respectively, of spin-coated **P1** films prepared from chloroform solutions as a function of film thickness.

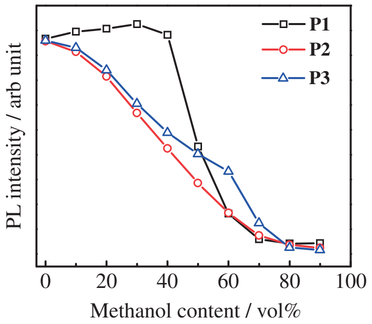


Figure 3. Dependence of PL intensities on the methanol content for **P1** (at 476 nm), **P2** (at 471 nm), and **P3** (at 471 nm) in chloroform/methanol mixtures (concentration; 5.0 × 10^{-3} mg mL^{-1}) at 20 °C.

of the twisted higher-order structure for **P2** was anticlockwise, while that for **P3** was clockwise, according to the exciton chirality theory.[15] The **P1** film exhibited Cotton effects due to its clockwise structure, which were relatively larger than those exhibited by **P2** and **P3** films with similar film thicknesses and optical absorbance. Negative Cotton effects were observed at 375 and 491 nm, while positive Cotton effects were observed at 443 and 467 nm. These observations are consistent with the maximum absorption peaks observed in the UV–vis absorption spectra. Figure 2a shows the photoluminescence (PL) and CPL spectra of a spin-coated **P1** film. The **P1** film exhibited a PL peak at 505 nm and a large negative CPL signal around the luminescence region. To the best of our knowledge, **P1** is the first polymer that exhibits an apparent CPL signal in the green region without external stimuli. In the differential scanning calorimetry (DSC) profile of **P1**, no transition peaks were observed, indicating that further annealing would not be effective for **P1**.

To quantitatively evaluate the CD and CPL properties of **P1**, the g_{abs} value at the lowest energy band for the CD spectrum (491 nm) and the g_{lum} value at the maximum luminescence wavelength for the CPL spectrum (505 nm) were calculated. Figure 2b shows the dependence of the g_{abs} value at 491 nm and the g_{lum} value at 505 nm on the thickness of **P1** spin-coated films. Both the $|g_{\text{abs}}|$ and $|g_{\text{lum}}|$ values increased nonlinearly with the film thickness. The $|g_{\text{abs}}|$ and $|g_{\text{lum}}|$ values for an 86-nm-thick **P1** film reached 0.3 and 0.2, respectively. Recently, Yu et al. reported that a hyperbranched poly(fluorenevinylene) derivative exhibited a high $|g_{\text{lum}}|$ value of 0.16 at 490 nm without an annealing process.[16] The pristine polymer films prepared by us that were thinner than 100 nm showed higher values in the green region, even without structure control for the suppression of excimer formation such as dendritic and hyperbranched structures.[17] Craig et al. reported that the $|g_{\text{abs}}|$ value of a thermally annealed chiral polyfluorene derivative was dependent on the film thickness, while the long-range correlation in the polymer nanoscopic orientation caused the dependence of the $|g_{\text{abs}}|$ value on the film thickness.[18] In contrast, Lakhwani et al.[19] reported that the g_{abs} and g_{lum} values of chiral polythiophene derivatives were not significantly dependent on the film thickness and that circular polarizations of absorption and luminescence for these polythiophenes originated at a molecular level. The film-thickness dependence of $|g_{\text{abs}}|$ and $|g_{\text{lum}}|$ implies that the chiroptical properties of **P1** may be attributed to the long-range correlation, similar to that for the chiral polyfluorene derivative reported by Craig et al.

To determine the dissymmetry factors for **P1**, the aggregation behaviors of the polymers in changing from solution to solid states were investigated. It is well-known that conjugated polymers exhibit PL quenching in good/poor solvent mixtures because of aggregation.[20] We attempted to monitor the aggregation behavior according to the decrease in the PL intensity at the maximum PL wavelength. Figure 3 shows plots of the PL intensity for **P1** (at 476 nm), **P2** (471 nm), and **P3** (471 nm) in chloroform (good solvent)/methanol (poor solvent) mixtures at a concentration of 5.0 × 10^{-3} mg mL^{-1} as a function of the methanol content at 20 °C. The PL intensities for **P2** and **P3** decreased at low methanol content (10 vol %), while that for **P1** remained constant up to a methanol content of 40 vol %, which indicates that **P2** and **P3** aggregated faster than **P1**. Thus, **P1** slowly formed an aggregate structure during the film-forming process. We consider that this slow aggregation process plays an important role in the efficient formation of higher-order chiral

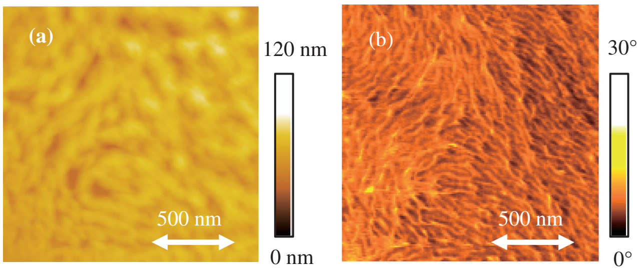


Figure 4. AFM (a) height and (b) phase images of **P1** aggregations prepared from 0.1 mg mL^{-1} chloroform solutions on a mica substrate.

structures. Other chiral conjugated polymers that exhibit a small CD signal, such as poly(phenyleneethynylene) and polythiophene derivatives, exhibit significant PL quenching at low content of the poor solvent.[20,21]

The nanostructure of films is important to understand the chiroptical properties of polymers.[22] Figure 4a shows an atomic force microscopy (AFM) image of the height of **P1** aggregations prepared from a 0.1 mg mL^{-1} chloroform solution on a mica substrate under a nitrogen atmosphere. Twisted fiber-like structures were observed in both height and phase images. There are related reports on the fiber-like structures of other chiral polyfluorene derivatives.[18,23]

From Figure 4b, the distance between the fiber-like structures was estimated to be approximately 10 nm, which is almost consistent with the fiber diameter of chiral fluorenes reported by Lakhwani et al.[24] The intensive chiroptical properties of nonannealed films could originate from either intramolecular chirality or an intermolecular chiral organization of chains in the fibrils.

In summary, we have demonstrated that the chiral π-conjugated polymer **P1** exhibits efficient CD and CPL signals in the green region without undergoing an annealing process or structural control. Different chiral substituents introduced at the 9 position of the fluorene unit resulted in slow aggregation for a favorable chiral conformation of chiral polyfluorene–thiophenes. The g_{abs} and g_{lum} values obtained for the **P1** films are the highest reported values in the green region at approximately 500 nm. The molecular design of these polymers will contribute to further increase in the g_{abs} and g_{lum} values, which will help in the development of 3D organic light-emitting diode (OLED) and CPL detectors.

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