

Circularly Polarized Photoluminescence of Two New Conjugated Polymers with Main Chain Chirality

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The circularly polarized photoluminescence spectra of two new chiral conjugated polymers with binaphthyl units are reported.

Owing to the potential applications for optical data processing¹ and display devices,² the development of new semiconducting polymers is of fundamental interest for several research groups. Moreover, the control of the linearly or circularly polarized light is also an important factor for these practical applications. Indeed, it has been shown that the electrical and optical properties of polymers depend on the conformation and/or the composition of the π -conjugated polymer chain. By introducing chirality into the conjugated polymers, the structural characteristics can be probed by chiroptical techniques, such as circular dichroism (CD) and circularly polarized luminescence (CPL) in the ground and excited state, respectively.³⁻⁶

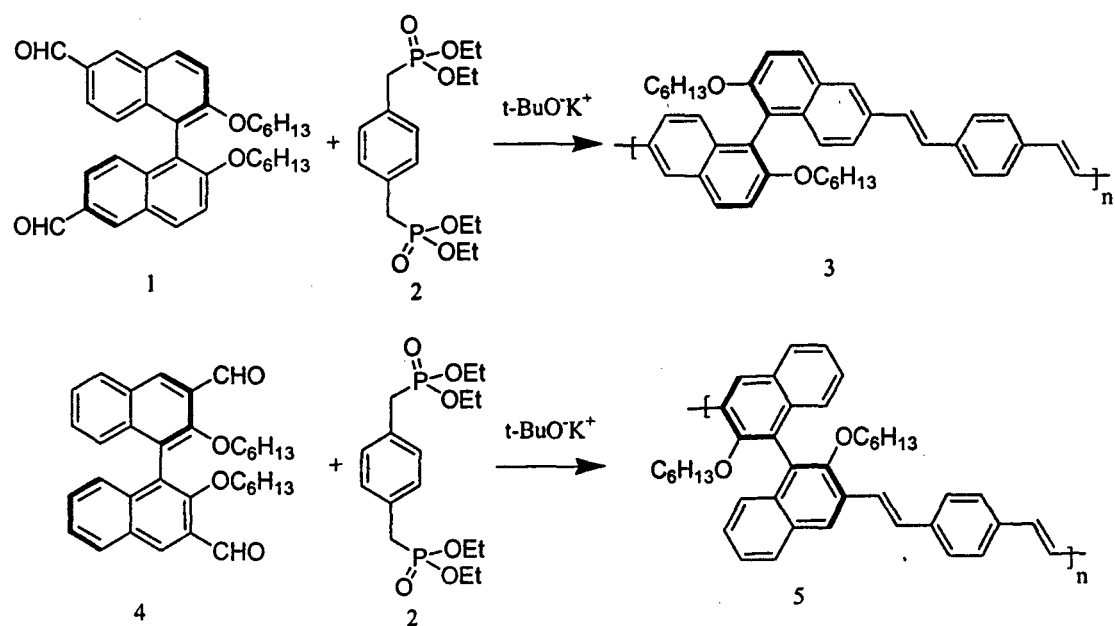
Circularly polarized photo- and electroluminescence have been first reported for polythiophene⁴ and poly(p-phenylene vinylene)⁵ with chiral pendants. The degree of circularly polarized luminescence, the dissymmetry factor, g_{lum} , defined as $g_{lum} = 2\Delta I/I = 2(I_L - I_R)/(I_L + I_R)$, where I_L and I_R refer, respectively, to the intensity of left and right circularly polarized light,³ was relatively low (1.3×10^{-3} for poly(p-phenylene vinylene), 5.0×10^{-3} for polythiophene).^{4,5} It should be mentioned that large values of degree of circularly polarized luminescence were reported in some liquid-crystalline systems such as chiral polyfluorenes derivatives (0.05, 0.16 or -0.25)⁶.

However, to date, the research of circularly polarized luminescence of polymers focuses on the conjugated polymers with chiral pendants. Circularly polarized

luminescence spectra of the conjugated polymers with main chain chirality have not been reported. As we know, conjugated polymers with chiral binaphthyl units have shown remarkable thermally stable chiral configuration⁷. Here we first report on the circularly polarized photoluminescence spectra of two new conjugated polymers with chiral binaphthyl units on the main chains.

The optically active poly{6,6'-[(R)-2,2'-dihexyloxy-1,1'-binaphthylene]-1,2-vinylene-1,4-phenylene-1,2-vinylene} (3) was prepared from (R)-2,2'-dihexyloxy-6,6'-diformyl-1,1'-binaphthalene (1) and 1,4-bis(diethylphosphinatyl methyl)-phenylene (2) with potassium t-butoxide as catalyst by Wittig-Horner condensation polymerization (Scheme 1)⁸. The achiral polymer has been studied as light-emitting diode⁹. The optically active poly{3,3'-[(R)-2,2'-dihexyloxy-1,1'-binaphthylene]-1,2-vinylene-1,4-phenylene-1,2-vinylene} (5) was prepared from (R)-2,2'-dihexyloxy-3,3'-diformyl-1,1'-binaphthalene (4) and the monomer 2 by the same method (Scheme 1). The key precursor 4 was prepared from (R)-2,2'-dihexyloxy-1,1'-binaphthyl according to alike literature method¹⁰. The polymers were purified by dissolving in chloroform and precipitating in methanol for three times. The polymers readily dissolve in common organic solvents, such as chloroform, THF, toluene and xylene. The specific optical rotation $[\alpha]_D^{20}$ of polymer 3 is -717° ($c=9.2 \times 10^{-4}$ g/ml, chloroform) and the specific optical rotation $[\alpha]_D^{20}$ of polymer 5 is -587° ($c=8.6 \times 10^{-4}$ g/ml, chloroform).

The number-average molecular weights were determined by gel permeation chromatography against the polystyrene standard to be 8443 with the polydispersity index of 3.40 for polymer 3 and 3065 with the polydispersity index of 3.26 for polymer 5.



Scheme 1. Syntheses of two optically active polymers

The UV/Vis absorption spectra (Figure 1) in chloroform display absorption maximums

at $\lambda_{\max} = 311\text{nm}$ and 374nm for the polymer 3 and at $\lambda_{\max} = 298\text{nm}$ and 370nm for the polymer 5 (Optical density at the absorption maximum is ~ 0.1). The circular dichroism (CD) spectra of two polymers in chloroform display very strong Cotton effects. The strong peaks at the shorter wavelength are due to the chiral binaphthyl units. The longer wavelength Cotton effect can be attributed to the chiral conjugation polymer chain. The degree of circular polarization in absorption, defined as $g_{\text{abs}} = (\epsilon_L - \epsilon_R) / \epsilon$, is on the order of 1×10^{-3} for polymer 3 and 2×10^{-3} for polymer 5 in chloroform at room temperature, respectively. These show that the two conjugated polymers have stable ordered conformations in chloroform at room temperature. This may be due to the helical structures of the two conjugated polymers containing chiral binaphthyl units.^{3,11} The circularly polarized luminescence and total luminescence spectra for two polymers in chloroform at room temperature when excited at $\lambda = 378\text{ nm}$ are plotted on Figure 1. The photoluminescence spectrum of the polymer 3 shows maximum emission at $\lambda = 458\text{ nm}$ with a shoulder peak at $\lambda = 439\text{ nm}$. The photoluminescence spectrum of the polymer 5 shows maximum emission at $\lambda = 457\text{ nm}$ with a shoulder peak at $\lambda = 429\text{ nm}$. The degree of circular polarization in emission has the same sign as g_{abs} on the high wavelength side. The magnitude of g_{lum} is on the order of approximately -1×10^{-3} for polymer 3 and approximately -2×10^{-3} for polymer 5, respectively.

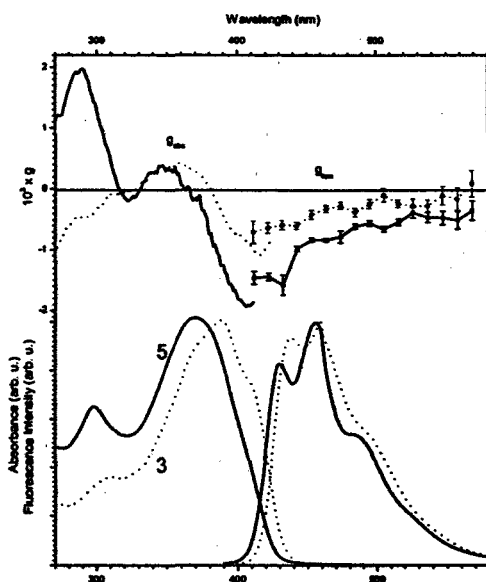


Figure 1. Top: Degree of circular polarization in absorption (g_{abs} , lines) and luminescence (g_{lum} , squares). The standard error for g_{lum} is indicated by the error bar. Bottom: Absorption and emission spectra ($\lambda_{\text{ex}} = 378\text{ nm}$) in chloroform at room temperature (polymer 3, dashed line; polymer 5, solid line)

Our results show that two new conjugated polymers with main chain chirality have

stable ordered conformations and can emit the circularly polarized light when excited in chloroform at room temperature.

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