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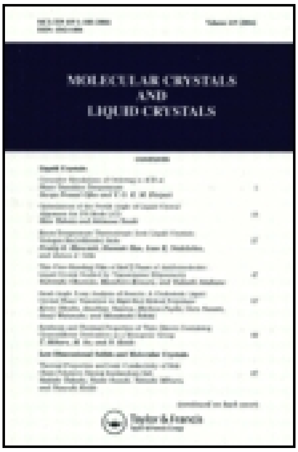

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Synthesis and Emission Behavior of Liquid-Crystalline Main-Chain Polyesters Containing Carbazole and Oxadiazole Moieties

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Synthesis and Emission Behavior of Liquid-Crystalline Main-Chain Polyesters Containing Carbazole and Oxadiazole Moieties

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Organic light-emitting diodes (OLEDs) based on chromophore-containing liquid crystals (LCs) can emit polarized light due to self-assembly of mesogenic chromophores. The stability of LC phases in LC polymers with a mesogenic group in the main chain is higher than that in the polymers containing a mesogenic group in the side chain.

In this study, a novel family of polyesters containing a carbazole moiety as a hole-transporting unit and an oxadiazole (OXD) moiety as an electron-transporting unit in the main chain, ***P10-DOXDCz*** *and* ***P16-DOXDCz****, were designed and synthesized. These polyesters were prepared by transesterification of* N*-hexyl-3,6-di[2-([1,3,4]oxadiazol-5-yl)-4-methylbenzoate]carbazole and 1,10-decanediol or 1,16-hexadecanediol at 220 °C for 20 h. They showed a nematic phase. Both* ***P10-DOXDCz*** *and* ***P16-DOXDCz*** *emitted intense blue fluorescence with a maximum at 439 nm and 450 nm in thin films, respectively, and their fluorescence quantum yields were 0.74 and 0.81 in solution, respectively. Both compounds exhibited polarized emission in a LC phases, and the order parameters estimated from the polarized emission spectra were 0.10 for* ***P10-DOXDCz*** *and 0.14 for* ***P16-DOXDCz****. Fabricated devices, ITO/PEDOT:PSS/****P10-DOXDCz*** *and* ***P16-DOXDCz****/MgAg, emitted blue light when a positive voltage was applied to the ITO electrode.*

Keywords Electroluminescence; polarized emission; carbazole; oxadiazole; main-chain liquid-crystalline polymer; bipolar

Introduction

Recently, much attention has been devoted to organic light-emitting diodes (OLEDs), which consist of electron-transporting, hole-transporting and emitting materials [1–4]. Among various materials, polymers are generally expected to be suitable for OLEDs because of their good processability and simple fabrication by solution processes, even though the efficiency of single-layer OLEDs is lower than that of multi-layer OLEDs. One useful approach for the fabrication of simple and efficient single-layer devices is to employ

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*Address correspondence to Dr. Motoi Kinoshita, Chemical Resources Laboratory, Tokyo Institute of Technology, R1-12, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan. Tel: (+81) 42-924-5241. Fax: (+81) 42-924-5275. E-mail: mkinoshita@res.titech.ac.jp polymers containing oxadiazole (OXD) as an electron-transporting moiety and carbazole as a hole-transporting moiety [5–11].

Liquid crystals (LCs) are ordered fluids, exhibiting anisotropic mechanical, electrical, magnetic and optical properties. Most of practical applications using LCs require control of molecular alignment on a substrate. Several low-molecular-weight LCs have been synthesized and investigated as electroluminescent (EL) materials. OLEDs using 2-(*p*-hexyloxybiphenyl)-5-(4-hexyloxyphenyl)-1,3,4-oxadiazole reported by Tsutsui *et al.* emitted light with a brightness of 0.8 cd/m^2 over a driving voltage of 280 V [12]. In the previous study, we evaluated the EL behavior of a cell containing 1,4-bis(*N,N*-diphenylaminophenyl-1,3,4-oxadiazolyl)benzene in a low-molecular-weight LC, 4-octyloxy-4′-cyanobiphenyl [13]. EL was observed at the LC state at a driving voltage of 135V [14, 15]. Poly(arylenevinylene) and polyfluorene (PF) derivatives reported by Wendorff *et al*. were explored in OLEDs by use of LC polymers with conjugated rigid rods and flexible alkyl spacers. The alkyl spacer allows easier molecular alignment in LC phases. For these polymers, maximum order parameters achieved in aligned layers were below 0.7.

We have previously synthesized a novel family of side-chain LC polymers containing an OXD and an amine or a carbazole moiety for OLEDs. These side-chain LC polymers showed bipolar character and functioned as polarized blue-emitting materials in OLEDs [11, 12]. In this study, we designed and synthesized a novel family of main-chain LC polymers with bipolar character, **P10-DOXDCz** and **P16-DOXDCz**, to enhance the stability of LC phases with a mesogenic group in the main chain.

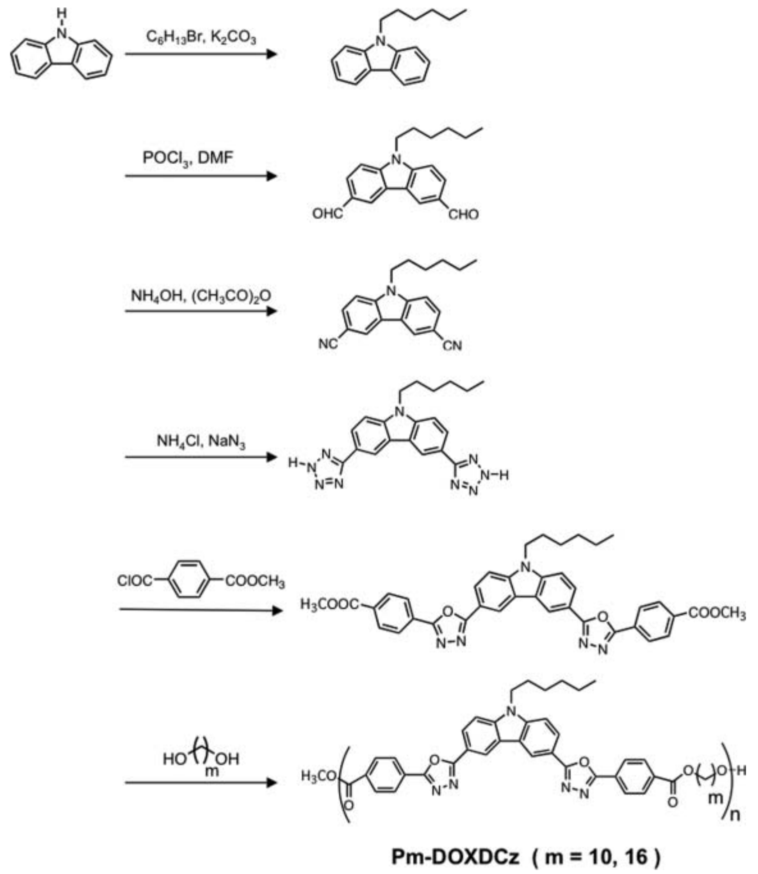
Experimental

The methyl ester containing the OXD and carbazole moieties, *N*-hexyl-3,6-di[2-([1,3,4]oxadiazol-5-yl)-4-methylbenzoate]carbazole, was prepared starting from carbazole by the synthetic route shown in Scheme 1. All reagents were purchased from Tokyo Kasei Co. Ltd. Kanto Kagaku Co. Ltd., and Aldrich Co. Ltd.. The compounds were identified by ^{1}H NMR (JEOL, GX300 (300 MHz)), elemental analysis and mass spectra (JMS-700 spectrometer with fast atom bombardment (FAB)). Molecular weight was determined by gel permeation chromatography (GPC; JASCO, model DG-980-50; column, Shodex GPC K802 + K804 + K805; eluent, chloroform) calibrated with standard polystyrenes. Absorption spectra were measured using a JASCO model U-550. Photoluminescence (PL) and EL spectra were obtained using a Hitachi F-4010 luminescence spectrometer. Fluorescence quantum yields of the polymers were determined by using quinine sulfate as a standard compound. LC and phase-transition behavior was examined on an Olympus BH-2 polarizing microscope equipped with Mettler hot-stage (FP-90 and FP-82). Thermotropic properties of LCs were determined with a differential scanning calorimeter (Seiko I&E, SSC-5200 and DSC220C) at a heating/cooling rate of 10 °C/min. The EL behavior was evaluated with an electrometer (Advantest R6243).

Synthesis

N-*Hexylcarbazole*

A mixture of carbazole (75.0 g, 450 mmol) and potassium carbonate (75.4 g, 545 mmol) in DMF (250 ml) was added into a 1-bromohexane (74.3 g, 450 mmol) followed by refluxing for 12 h. The crude product was extracted with chloroform and washed water. The product



Scheme 1. Synthetic route of the polymers used in this study.

was purified by silica gel column chromatography with an eluent of ethyl acetate/*n*-hexane. Yield: 62.1 g, 55%. ^{1}H NMR (δ, $CDCl_3$): 0.74–0.81 (*t*, 3H), 1.16–1.29 (*m*, 6H), 1.74–1.79 (*m*, 2H), 4.13–4.18 (*t*, 2H), 7.09–7.38 (*m*, 6H), 7.98–8.01 (*d*, 2H), 8.32–8.35 (*s*, 2H). *Anal. Calcd. for* $C_{18}H_{21}N$: C, 86.01%; H, 8.42%; N, 5.57%. *Found.* C, 86.13%; H, 8.51%; N, 5.67%.

N-*Hexyl-3,6-diformylcarbazole*

Phosphoryl chloride (91.2 g, 595 mmol) was added slowly into DMF (43.5 g, 595 mmol), which was purged with nitrogen and cooled to 0 °C. The reactant was warmed to room temperature and stirred for 1 h and cooled again to 0 °C. This mixture was added to a solution of *N*-hexylcarbazole (30.0 g, 119 mmol) in 1,2-dichloroethane (100 ml) and the resulting mixture was kept at 90 °C for 48 h. The crude product was poured into ice water and extracted with chloroform and washed water. The product was purified by silica gel column chromatography with an eluent of ethyl acetate/*n*-hexane and recrystallized from methanol. Yield: 2.17 g, 22%. ^{1}H NMR (δ, $CDCl_3$): 0.82–0.87 (*t*, 3H), 1.24–1.53 (*m*, 6H), 1.85–1.95 (*m*, 2H), 4.35–4.37 (*t*, 2H), 7.52–7.55 (*d*, 2H), 8.06–8.09 (*d*, 2H), 8.66 (*s*, 2H), 10.12 (*s*, 2H). *Anal. Calcd. for* $C_{20}H_{21}NO_2$: C, 78.15%; H, 6.89%; N, 4.56%. *Found.* C, 78.08%; H, 7.14%; N, 4.54%.

N-*Hexyl-3,6-dicyanocarbazole*

A mixture of *N*-hexyl-3,6-diformylcarbazole (2.01 g, 6.51 mmol), hydroxylamine hydrochloride (2.10 g, 32.5 mmol), acetic anhydride (3.32 g, 32.5 mmol), pyridine (2.57g, 32.5 mmol) and DMF (50ml) was stirred and heated at 140 °C for 8 h. The crude product was extracted with chloroform and washed water. The product was purified by silica gel column chromatography with an eluent of chloroform and recrystallized from hexane/ethanol. Yield: 1.61 g, 83%. ^{1}H NMR (δ, $CDCl_3$): 0.82–0.95 (*t*, 3H), 1.20–1.56 (*m*, 6H), 1.81–1.88 (*m*, 2H), 4.31–4.36 (*t*, 2H), 7.49–7.56 (*d*, 2H), 7.75–7.8 (*d*, 2H), 8.32–8.35 (*s*, 2H). *Anal. Calcd. for* $C_{20}H_{19}N_3$: C, 79.70%; H, 6.35%; N, 13.94%. *Found.* C, 79.25%; H, 6.80%; N, 13.60%.

N-*Hexyl-3,6-ditetrazolylcarbazole*

A mixture of *N*-hexyl-3,6-dicyanocarbazole (1.3 g, 4.31 mmol), sodium azide (0.84 g, 12.9 mmol), ammonium chloride (0.7 g, 12.9 mmol) and DMF (20 ml) was stirred and heated at 140 °C for 10 h. The cooled solution was slowly poured into water. Recrystallization from chloroform/methanol gave the desired product. Yield: 1.67 g, 75%. ^{1}H NMR (δ, DMSO): 0.77–0.87 (*t*, 3H), 1.15–1.33 (*m*, 6H), 1.76–1.86 (*m*, 2H), 4.21–4.31 (*t*, 2H), 7.33–7.45 (*d*, 2H), 7.73–7.74 (*d*, 2H), 8.32–8.35 (*s*, 2H). *Anal. Calcd. for* $C_{20}H_{21}N_9$: C, 62.0%; H, 5.46%; N, 32.54%. *Found.* C, 62.50%; H, 5.70%; N, 32.22%.

N-*Hexyl-3,6-di[2-([1,3,4]oxadiazol-5-yl)-4-methylbenzoate]carbazole*

A mixture of *N*-hexyl-3,6-ditetrazolylcarbazole (1.6 g, 4.13 mmol), terephthalic acid monomethyl ester chloride (8.2 g, 41.3 mmol) and pyridine (20 ml) was stirred and heated at 140 °C for 24 h. The cooled solution was slowly poured into dilute hydrochloric acid. The crude product was extracted with chloroform and washed water. The product was purified by silica gel column chromatography with an eluent of chloroform/THF and recrystallized from chloroform/methanol. Yield: 1.3 g, 46%. ^{1}H NMR (δ, $CDCl_3$): 0.84–0.88 (*t*, 3H), 1.20–1.38 (*m*, 8H), 1.88–1.92 (*m*, 2H), 3.95–3.96 (*s*, 6H) 4.19–4.34 (*t*, 2H), 7.47–7.49(*d*, 2H), 8.15–8.22 (*d*, 10H), 8.80–8.82 (*s*, 2H). MS (FAB): 656 (MH^+). *Anal. Calcd. for* $C_{38}H_{33}N_5O_6$: C, 69.61%; H, 5.07%; N, 10.68%; O, 14.64%. *Found.* C, 69.70%; H, 5.34%; N, 10.66%; O, 14.57%.

P10-DOXDCz or P16-DOXDCz

A mixture of *N*-hexyl-3,6-di[2-([1,3,4]oxadiazol-5-yl)-4-methylbenzoate]carbazole (1.0 g, 1.53 mmol), 1,10-decanediol (0.32 g, 1.83 mmol) or 1,16-hexadecanediol (0.47 g, 1.83 mmol) and di-*n*-butyltin oxide as a catalyst was stirred and heated at 200 °C for 2 h under nitrogen atmosphere. Then, the temperature of the polymerization mixture was slowly raised to 220 °C and then kept for 48 h under vacuum (5 mmHg). The obtained polymer was purified by reprecipitation from chloroform and methanol three times [16,17]. Yield: **P10-DOXDCz**, 0.6 g (51%); **P16-DOXDCz**, Yield: 0.4 g (31%).

Results and Discussion

LC Behabior

Both polymers exhibited a nematic phase. Figure 1 shows polarizing microphotographs of **P10-DOXDCz** and **P16-DOXDCz**. Upon heating, the baseline shift due to glass transition temperature (T_g) of **P10-DOXDCz** and **P16-DOXDCz** was observed at around 137 °C and 87 °C, respectively, and endothermic peaks for the LC-isotropic phase transition appeared at around at 182 °C and 157 °C, respectively. T_gs and phase transition temperatures are summarized in Table 1.

Optical Properties

Figure 2 shows the absorption and fluorescence spectra of **P10-DOXDCz** and **P16-OXDCz** in thin films. **P10-DOXDCz** and **P16-DOXDCz** exhibited maximum absorption wavelength at 358 nm and 353 nm and blue fluorescence with an emission peak at 439 nm and 450 nm, respectively.

The fluorescence quantum yield is an important factor to evaluate the suitability of compounds for OLEDs. The fluorescence quantum yields of **P10-DOXDCz** and **P16-DOXDCz** in chloroform were found to be 0.74 and 0.81, respectively.

Polarized Emission

The aligned thin films of **P10-DOXDCz** and **P16-DOXDCz** were prepared by a rubbing technique. A preferential alignment was induced in the polyesters coated onto a rubbed glass substrate. The films were annealed for 1 h at the temperature where the polymers showed a nematic phase and cooled to glassy state. Polarized absorption and PL spectra were measured to estimate the degree of alignment of the main chain as shown in Figure 3. The order parameter can be determined by the following equation:

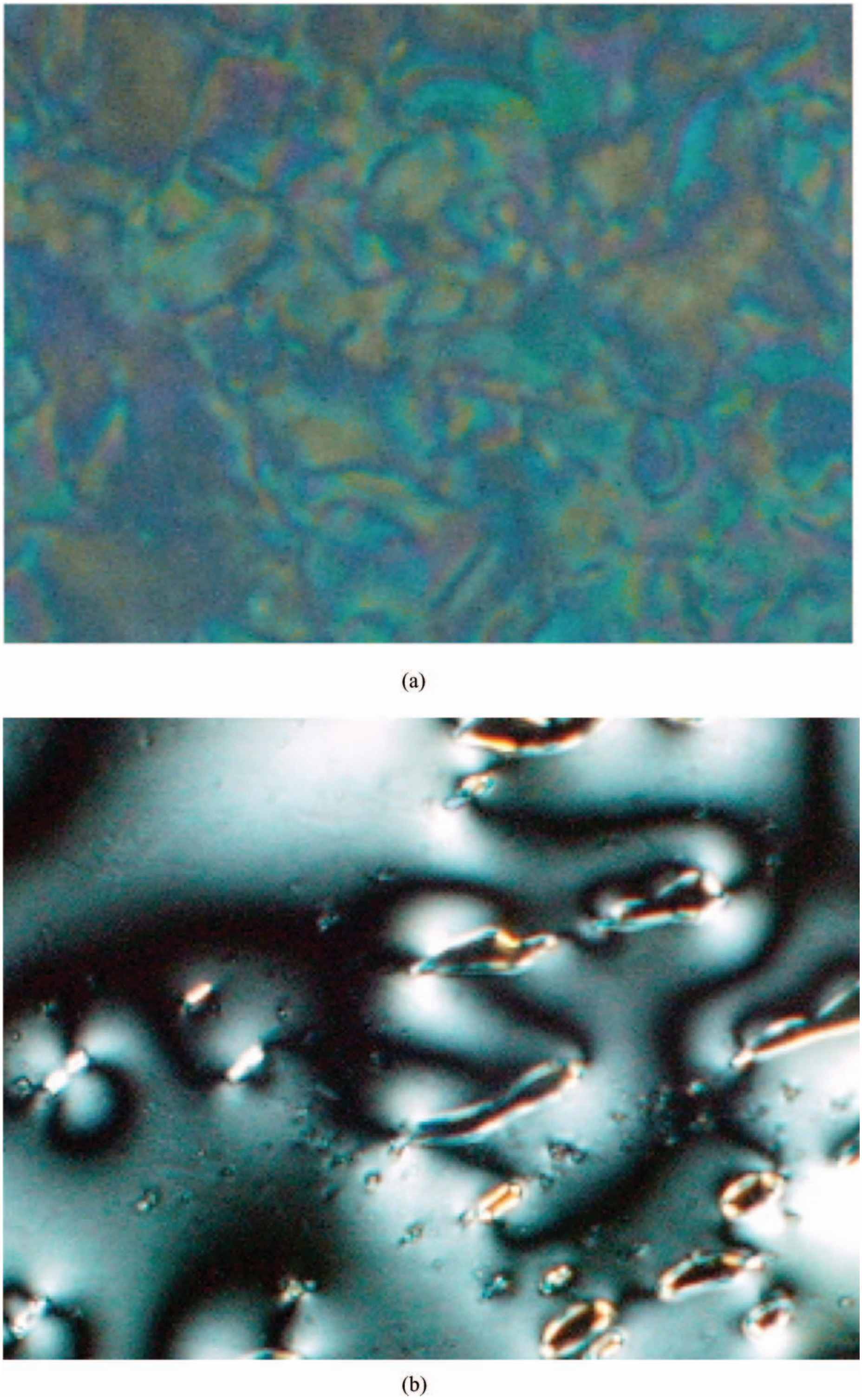
$$S = \frac{R-1}{R+2} \tag{1}$$

where $R = A_{\parallel}/A_{\perp}$ is a dichroic ratio with $A_{\parallel}$ and $A_{\perp}$ being the values of the polarized absorption and PL parallel and perpendicular to the rubbing direction. The order parameters (S) and dichroic ratio (R) of **P10-DOXDCz** and **P16-DOXDCz** were $S = 0.10$ and 0.14, $R = 1.33$ and 1.47, respectively. Thus, these polymers were found to show dichroism.

Table 1. Phase transition temperatures and molecular weights of the LC polymers used in this study[a]

Polymer	M_n	M_w/M_n	Phase transition temperature (°C)
P10-DOXDCz	20,000	24.6	G 137 N 182 I
P10-DOXDCz	4,000	3.04	G 87 N 157 I

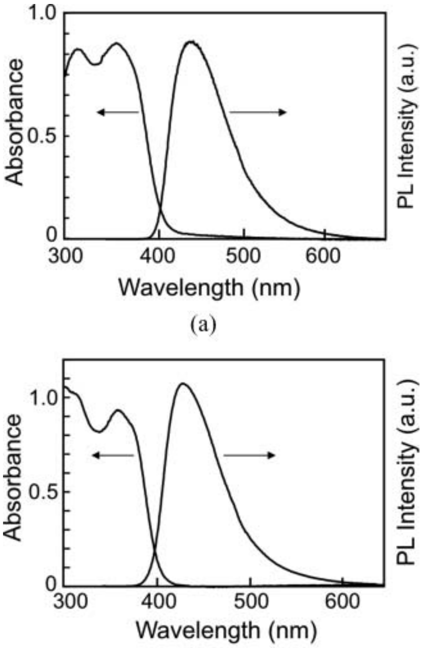
[a] Abbreviations: G, glassy; N, nematic; I, isotropic; M_n, number-average molecular weight; M_w, weight- average molecular weight.



(a)

(b)

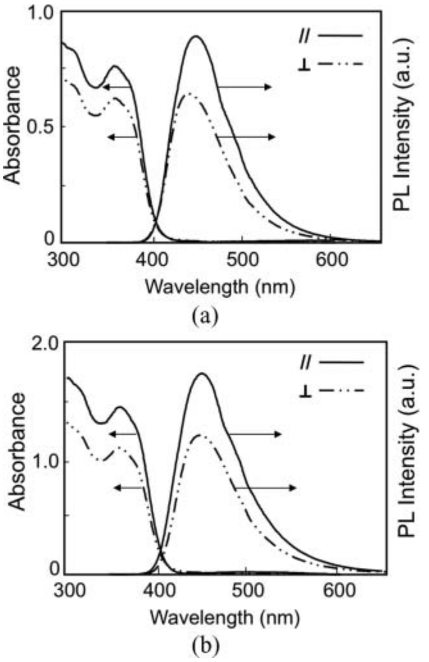
Figure 1. Polarizing optical micrographs of **P10-DOXDCz** at 160 °C (A) and **P16-DOXDCz** at 140 °C (B).



(a)

(b)

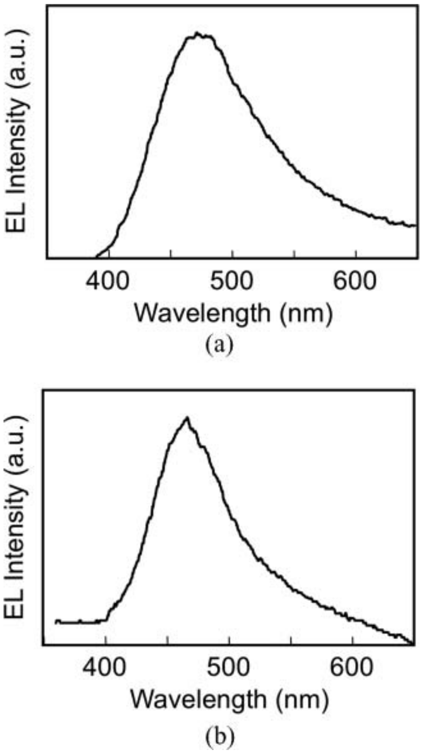
Figure 2. Absorption and PL spectra of **P10-DOXDCz** (a) and **P16-DOXDCz** (b) in thin films.



(a)

(b)

Figure 3. Polarized absorption and PL spectra of **P10-DOXDCz** (a) and **P16-DOXDCz** (b) aligned on a rubbed glass substrate. (‖) Parallel to the rubbing direction; (⊥) perpendicular to the rubbing direction.



(a)

(b)

Figure 4. EL spectra of ITO/PEDOT:PSS/**P10-DOXDCz**/MgAg (a) and ITO/PEDOT:PSS /**P16-DOXDCz**/MgAg (b).

Electroluminescence

We also fabricated devices using **P10-DOXDCz** or **P16-DOXDCz** as an emitter, ITO/PEDOT:PSS/**P10-DOXDCz**/MgAg and ITO/PEDOT:PSS/**P16-DOXDCz**/MgAg. To accelerate the hole-injection from an anode into the emitter, PEDOT:PSS was spin-coated onto an ITO-coated glass substrate. Then, the polymer film was spin-coated from a 1.5 wt% chloroform solution onto the PEDOT:PSS film and an alloy of Mg and Ag (volume rate 10:1) as a cathode was deposited onto the polymer film. The fabricated devices with both polymers emitted blue light when a positive voltage was applied to the ITO electrode. Figure 4 shows the EL spectra of the devices. **P10-DOXDCz** and **P16-DOXDCz** showed a blue emission peak at 470 nm and 468 nm, respectively. Hence the polymers functioned as blue emitters in OLEDs.

Conclusion

Novel liquid-crystalline polyesters containing a carbazole moiety as a hole-transporting unit and an oxadiazole moiety as an electron-transporting unit in the main chain, **P10-DOXDCz** and **P16-DOXDCz**, were designed and synthesized, and they showed a nematic LC phase. Both polyesters emitted intense blue fluorescence with a maximum at 439 nm and 450 nm in thin films, and their fluorescence quantum yields were 0.74 and 0.81 in solution, respectively. Polarized fluorescence was observed in a LC phase, and order parameters estimated by the polarized emission were 0.10 and 0.14 for **P10-DOXDCz** and **P16-DOXDCz**, respectively. Double-layer device using **P10-DOXDCz** and **P16-DOXDCz** as emitters, ITO/PEDOT:PSS/**P10-DOXDCz** or **P16-DOXDCz**/MgAg, were fabricated. The fabricated devices emitted blue light.

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