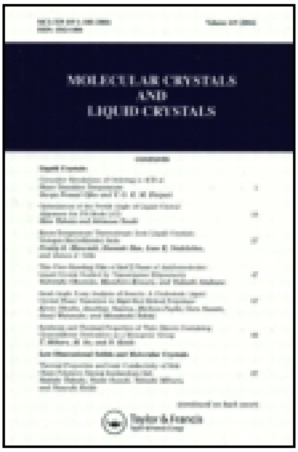

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Polarized Emission Behavior of Pt Complex-Doped Polymer Films

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Polarized Emission Behavior of Pt Complex-Doped Polymer Films

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Organic light-emitting diodes (OLEDs) based on conjugated polymers exhibiting polarized emission have attracted much attention because of their potential as backlights for conventional liquid crystal (LC) displays and 3-D displays. We have reported a new series of LC polymers based on donor-acceptor architecture containing an oxadiazole (OXD) and several amine moieties in the same side chain, which exhibit bipolar character with a wide energy band gap.

In this study, to develop phosphorescent OLEDs with polarized emission, we synthesized a platinum complex, Pt(4-decyloxy)salen, with emitting property, and fabricated the device consisting of Pt complex as a guest and LC polymers as a host material. The Pt complex exhibited high thermal stability, good solubility and an emission peak at 530 nm in dichloromethane. To obtain electroluminescense from the Pt complex, we fabricated ITO/rubbed PEDOT:PSS/Pt(4-decyloxy)salen:host polymer/MgAg devices. The devices emitted a yellowish green light, which was dominated by the triplet emission of the platinum complex. In addition, polarized electroluminescence was observed in an aligned LC polymer film.

Keywords Electroluminescence; platinum complex; polarized emission

Introduction

Organic light-emitting diodes (OLEDs) have recently received a great deal of attention for their application as full-color, flat-panel displays as well as from the standpoint of scientific interest [1–4]. They are attractive because of low-voltage driving, high brightness, capability of multi-color emission by the selection of emitting materials and easy fabrication of large-area and thin-film devices. In addition, OLEDs exhibiting polarized emission have attracted much attention because of their potential as backlights for conventional liquid crystal (LC) displays and 3-D displays [5–10].

Recently, OLEDs based on phosphorescent materials such as Ir complexes and bipolar host materials, have shown high efficiency [11–20]. To develop high performance OLEDs, not only efficient emitting material but also bipolar host materials with wide energy band gaps are required. The host materials used for OLEDs should meet the requirements of

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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 energy level matching for charge carrier injection and acceptance of both holes and electrons in a nano-layered film, and hence should desirably possess bipolar character to permit the formation of both stable cation and anion radicals.

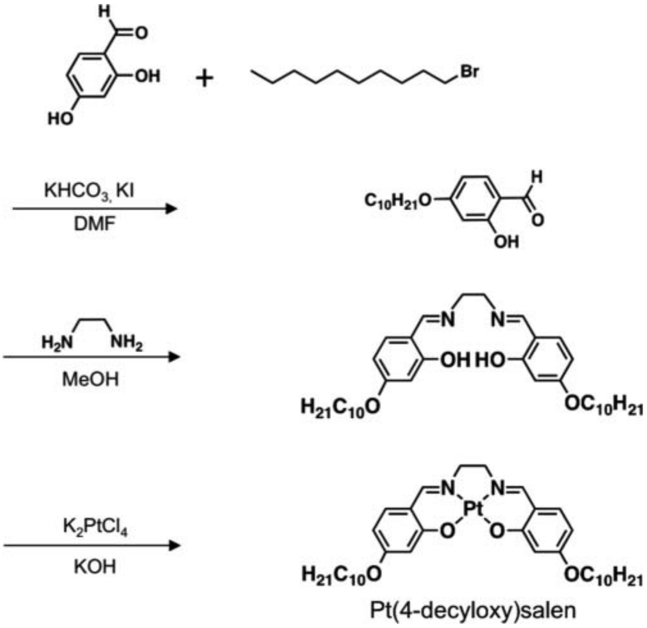
Previously, we synthesized LC polymers containing oxadiazole and amine moieties in the same side chain [21–25]. They showed LC behavior, high quantum efficiency and polarized blue emission. Furthermore, LC polymers had a wide band-gap and bipolar charge-transporting ability. However, these LC polymers emitted fluorescence, due to which at most 25% of the excitation states generate light. In this study, we prepared a phosphorescent Pt complex-doped LC host polymer and investigated its photo- and electroluminescent behavior.

Experimental

Synthesis

N,N′-Bis(4-*n*-decyloxy-salicylaldehydo)ethylenediaminateplatinum(II)complex (Pt(4-decyloxy)salen) was prepared starting from 2,4-dihydroxybenzaldehyde 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 synthesized compounds were identified by ^{1}H NMR (JEOL, GX300 (300 MHz)), elemental analysis and mass spectra (JMS-700 spectrometer with fast atom bombardment (FAB)).

Synthesis of 4-(decyloxy)salicylaldehyde (1). 2,4-Dihydroxybenzaldehyde (6.9 g, 50 mmol), 1-bromodecane (11.2 g, 51 mmol), $KHCO_3$ (5.2 g, 52 mmol) and a trace amount of KI were added to DMF (70 ml). The resulting mixture was stirred at 135°C for 4 h. After



Scheme 1. Synthetic route of the Pt complex.

being cooled to room temperature, the mixture was poured into 1N HCl *aq.* and extracted with chloroform, and the organic layer was evaporated to dryness. After evaporation of the solvent, the residue was purified by column chromatography on silica gel (ethyl acetate : hexane = 9 : 1) to yield colorless oil. Yield: 10 g, 72%; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.86 (*t*, 3H, $J = 6.7$ Hz), 1.18-1.55 (*m*, 16H), 1.78 (*q*, 2H, $J = 7.0$ Hz), 3.97 (*t*, 2H, $J = 6.6$ Hz), 6.94 (*d*, 1H, $J = 9.0$ Hz), 7.39 (*t*, 1H, $J = 3.1$ Hz), 7.52 (*dd*, 2H, $J = 9.1$ Hz, 3.1 Hz), 10.3 (*s*, 1H). Mass (FAB) found: m/z 279 $[M]^+$ (278.19 *calcd. for* $C_{17}H_{26}O_3$).

Synthesis of N,N′*-bis(4-decyloxysalicylidene)ethylenediamine (2).* 2-Hydroxy-4-decyloxybenzaldehyde (9.8 g, 34 mmol) and ethylenediamine (1.0 g, 17 mmol) were added to ethanol (50 ml), and the mixture was stirred and refluxed for 30 min under argon. The Schiff-base ligand was separated as a yellow solid and was washed with H_2O, methanol and ethanol. Yield: 4.2 g, 43%; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.86 (*t*, 6H, $J = 7.0$ Hz), 1.15–1.48 (*m*, 32H), 1.74 (*q*, 4H, $J = 6.7$ Hz), 3.83 (*s*, 4H) 3.92 (*t*, 4H, $J = 6.6$ Hz), 6.22 (*dd*, 2H, $J = 9.0$ Hz, 3.1Hz), 6.69 (*d*, 2H, $J = 6.7$ Hz), 7.08 (*d* 2H), 8.17 (*s*, 2H). Mass (FAB) found: m/z 580 $[M]^+$ (580.42 *calcd. for* $C_{36}H_{56}N_2O_4$).

Synthesis of Pt(4-decyloxy)salen. $K_2[PtCl_4]$ (3.0 g, 7.2 mmol) and *N,N*′-bis(4-decyloxysalicylidene)ethylene-diamine (8.3 g, 14 mmol) were added to 1M of KOH *aq.* and the mixture was stirred and heated at 40°C for 24 h under argon. The reaction mixture was evaporated and purified by flash column chromatography (dichloromethane). The product was evaporated to dryness. The yellow solid was recrystallized from dichloromethane, and dried in *vacuo* to obtain orange powder. Yield: 0.6 g, 10%; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.86 (*t*, 6H, $J = 7.0$ Hz), 1.25-1.72 (*m*, 32H), 3.71 (*s*, 4H), 3.92 (*t*, 4H, $J = 6.6$ Hz), 6.22 (*dd*, 2H, $J = 6.3$ Hz, 3.8 Hz), 6.69 (*d*, 2H, $J = 2.4$ Hz), 7.08 (*d*, 2H, $J = 8.1$ Hz), 7.82 (*s*, 2H). Mass (FAB) found: m/z 773 $[M]^+$ (773.37 *calcd. for* $C_{36}H_{54}N_2O_4Pt$). *Anal. calcd. for* $C_{36}H_{54}N_2O_4Pt$: C, 55.87; H, 7.03; N, 3.62; O, 8.27; Found: C, 55.64; H, 6.86; N, 3.44; O, 8.44.

Molecular Properties of Pt(4-decyloxy)salen

Thermal properties of the compound were determined with an Olympus BH-2 polarizing microscope equipped with Mettler hot-stage (FP-90 and FP-82), and a differential scanning calorimeter (Seiko I&E, SSC-5200 and DSC220C) at a heating/cooling rate of 3°C/min. Electronic absorption spectra were measured using a JASCO U-550 spectrophotometer. Photoluminescence (PL) and EL spectra were obtained using a Hitachi F-7000 luminescence spectrometer. Fluorescence quantum yields of the polymers were determined by using quinine sulfate as a standard compound.

Figure 1 shows DSC curves of Pt(4-decyloxy)salen. When a crystalline sample was heated, two endothermic peaks were observed at 69°C and 114°C. Upon further heating, it melted at 233°C to yield an isotropic liquid. No mesophase was observed, even on cooling. This was supported by XRD patterns (Figure 2). Figure 3 shows the electronic absorption and PL spectra of Pt(4-decyloxy)salen in a dichloromethane solution. The electronic absorption spectrum of the Pt complex shows bands peaking at 315, 330 and 400 nm. The absorption peaks at 315 and 330 nm are due to typical ligand-centered $\pi\pi^*$ transition, and another absorption band at 400 nm may be assigned probably to metal-to-ligand charge transfer (MLCT). The Pt complex exhibited green phosphorescence with a maximum peak at 534 nm ($\phi_{em} = 0.36$) at room temperature.

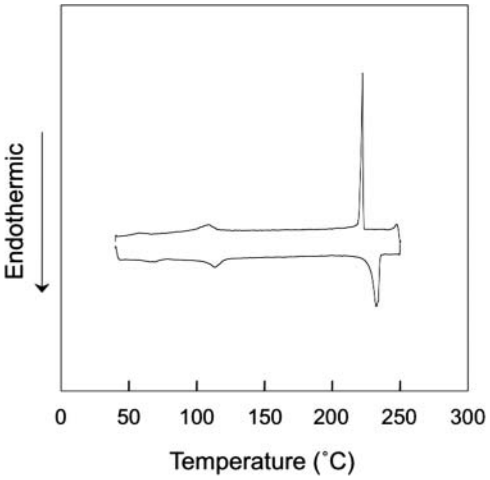


Figure 1. DSC thermograms of the Pt complex.

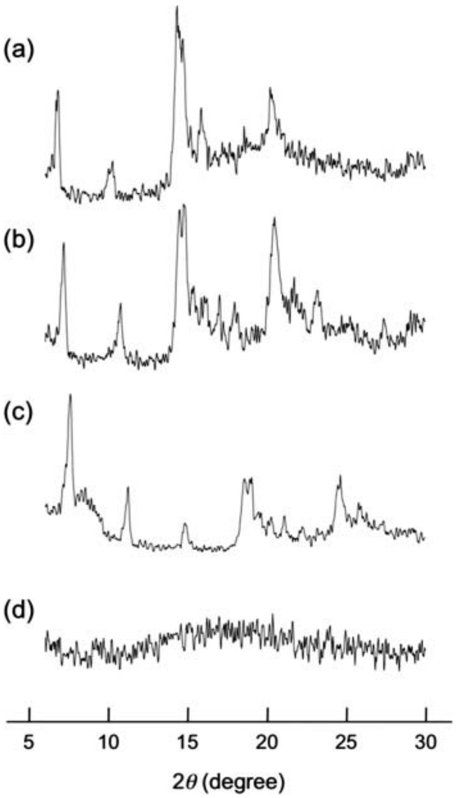


Figure 2. XRD patterns of the Pt complex at several temperatures; (a) 55°C, (b) 85°C, (c) 170°C, (d) 250°C.

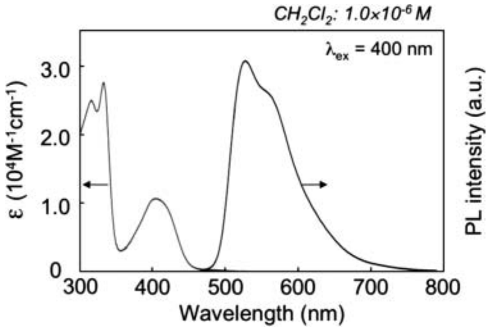


Figure 3. UV-vis absorption and photoluminescent spectra of the Pt complex in dichloromethane.

Polarized Emission Behavior

Polarized PL spectra of the Pt(4-decyloxy)salen doped in an LC host were measured to explore anisotropic emission behavior of the Pt complex. The LC cell was prepared as follows. S1114 and 0.1 mol% of Pt(4-decyloxy)salen were dissolved separately in dichloromethane and the solutions were mixed together. After the solvent was removed completely under vacuum, the LC mixture was sandwiched between two parallel transparent glass substrates with a gap of 20 μm by silica particles as a spacer. The inner surfaces of the two substrates were coated with rubbed PEDOT:PSS to obtain homogeneous alignment of LCs. The monodomain structure of the LC cell was confirmed by polarizing optical microscopy (POM), and homogeneous alignment was observed.

Figure 4 shows the polarized PL spectra of the LC cell. The emission intensity of the aligned film turned out to be high along the rubbing direction and low in the direction perpendicular to it, yielding dichroic ratio (R_{PL}) of 1.7 at 550 nm ($R_{\mathrm{PL}} = A_{\|}\mathrm{A} \perp$ is a

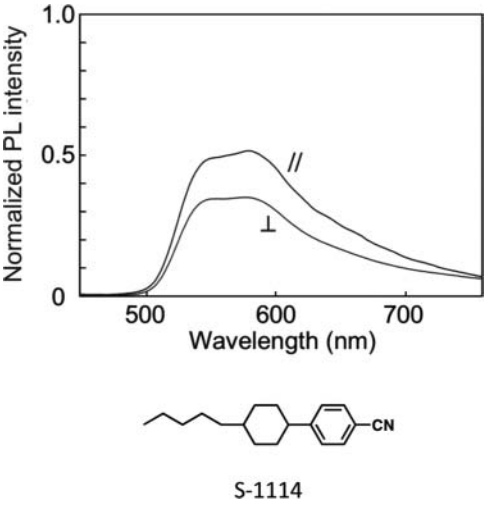


Figure 4. Polarized photoluminescent spectra of the Pt complex doped S-1114 in the homogeneous LC cell at a concentration of 0.10 mol% ($\lambda_{\mathrm{ex}} = 400$ nm). (//) Parallel to the rubbing direction; (⊥) perpendicular to the rubbing direction.

dichroic ratio with $A_{\parallel}$ and $A_{\perp}$ being the values of the polarized absorption parallel and perpendicular to the rubbing direction). Thus, the Pt complex is expected to function as a polarized emitter with a suitable electron conducting host polymer for OLEDs.

OLED

Figure 5 shows the PL spectra and molecular structures of PVK as an amorphous host polymer and **PA6CB** as an LC host polymer. To fabricate the OLED, Pt(4-decyloxy)salen doped host polymer films were obtained by spin-coating on an ITO coated glass substrate covered with rubbed PEDOT:PSS at a rate of 2500 rpm for 30 s with 1,1,2,2-tetrachloroethane polymer solutions at several concentrations of Pt complex. Film thicknesses were determined by a Dektak surface profiler. An alloy of magnesium and silver (volume ratio: *ca.* 10:1) was vacuum deposited onto the polymer layer by simultaneous evaporation from two separate sources. The EL behavior was evaluated with a DC voltage current source monitor (Advantest R6243) and a fluorescence spectrometer (Hitachi F7000).

Figure 6 shows the EL spectra of the fabricated devices using Pt(4-decyloxy)salene-doped **PVK** and **PA6CB** as host polymers. The devices emitted yellowish-green light peaking at around 580 nm, which mainly originates from Pt(4-decyloxy)salen. A very weak emission with λ_{max} at approximately 600 nm was observed, which may result from exciplex formed by the Pt complex and host polymers, respectively.

Figure 7 shows the polarized EL spectrum of the device, ITO/rubbed PEDOT:PSS/Pt complex doped LC Polymer/MgAg. The EL intensity of the aligned film turned out to be

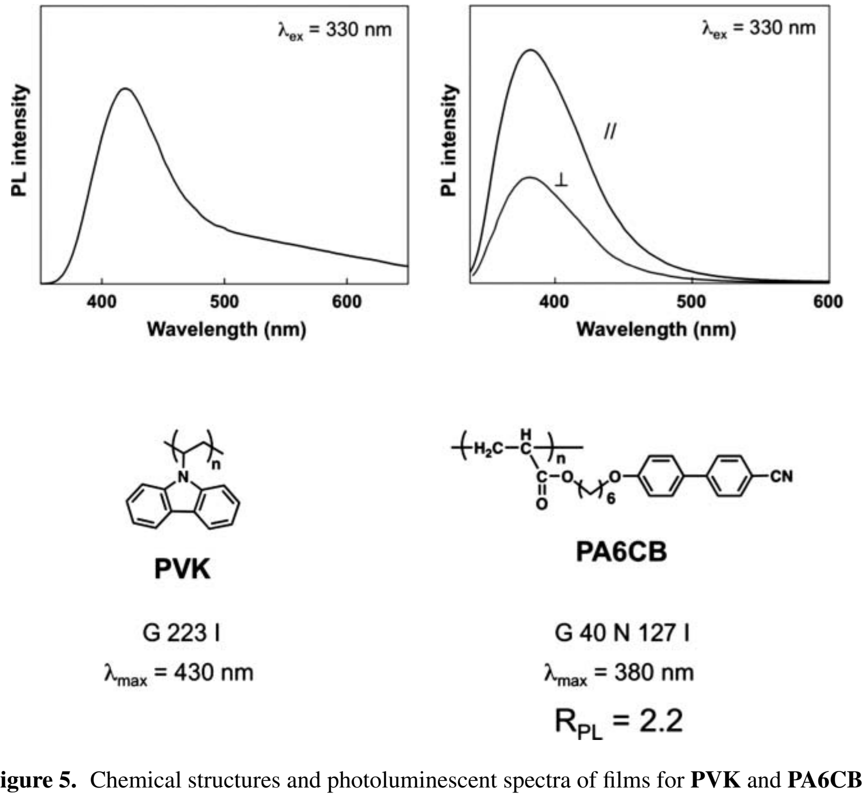


Figure 5. Chemical structures and photoluminescent spectra of films for **PVK** and **PA6CB**.

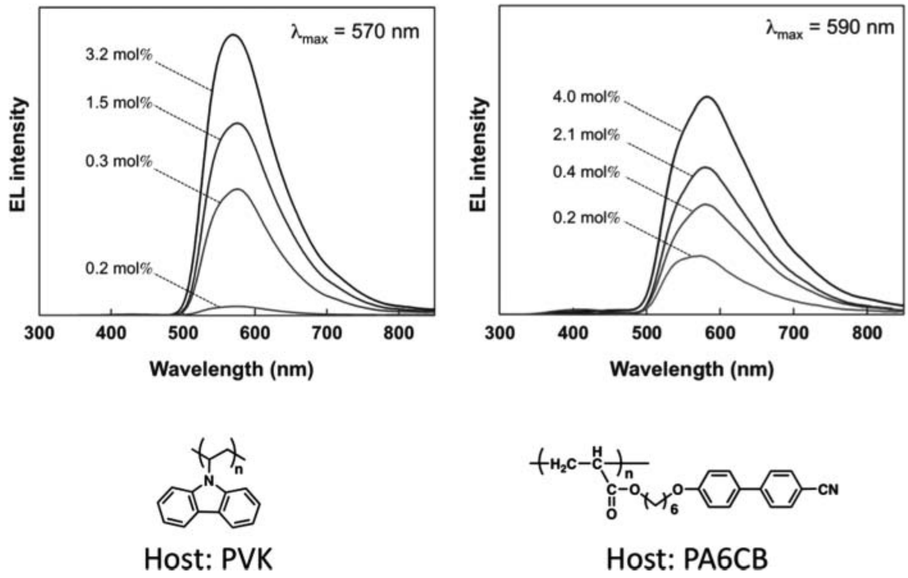


Figure 6. Electroluminescent spectra of the Pt complex-doped **PVK** and **PA6CB** devices at various concentrations.

higher along the rubbing direction. The dichroic ratio calculated from the polarized EL spectra was $R_{EL} = I_{\|}/I_{\perp} = 2.4$ where R_{EL} is a dichroic ratio with $I_{\|}$ and $I_{\perp}$ being the values of polarized emission parallel and perpendicular to the rubbing direction. When the device was fabricated using PVK as a host polymer, the EL spectrum was polarization-independent

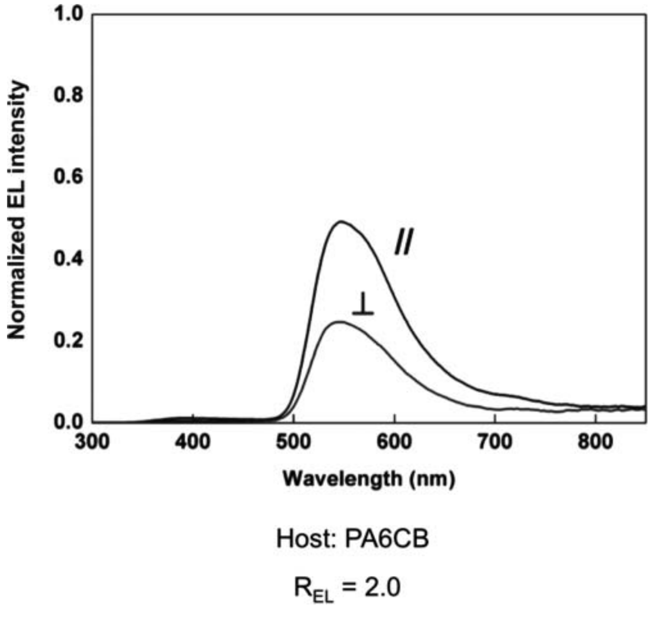


Figure 7. Polarized EL spectra of the Pt complex-doped **PA6CB** device at the concentration of 4.0 mol%. (//) Parallel to the rubbing direction; (⊥) perpendicular to the rubbing direction.

because the Pt complex is not aligned in the amorphous host polymer. Thus, the Pt complex was found to function as a polarized phosphorescent material for polarized OLEDs with the combination of the aligned host polymer.

Conclusions

In this study, we synthesized Pt complex as a phosphorescent material and fabricated the device consisting of Pt complex doped in an LC polymer to develop a polarized phosphorescent OLED. The synthesized Pt complex showed high thermal stability, good solubility and green emission in solution. The fabricated device using Pt complex doped in host polymers emitted yellowish-green light, which is dominated by the triplet emission of the platinum complex. In addition, the polarized EL spectrum was observed in an aligned LC polymer film. Thus, as polarized OLEDs are of great interest due to their potential use in efficient light sources for liquid crystal displays and three-dimensional displays, this study suggests a way to achieve such polarized phosphorescence using an aligned metal complex.

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