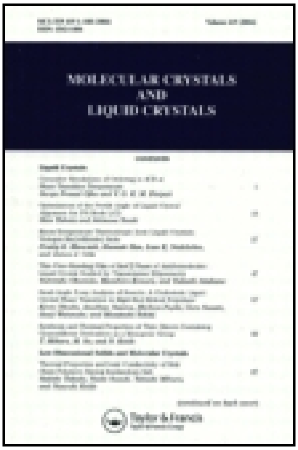

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Synthesis and Luminescent Properties of Poly(alkylated indenopyrazine) and Its Copolymer Containing an Alkylated Spirofluorene Moiety

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Synthesis and Luminescent Properties of Poly(alkylated indenopyrazine) and Its Copolymer Containing an Alkylated Spirofluorene Moiety

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We have synthesized new alkylated indenopyrazine homopolymer and its copolymer having an alkylated spirofluorene moiety. Poly(6,6,12,12-(Tetra-2-ethylhexyl)-6,12-Dihydrodiindeno[1,2-b:1,2-e]pyrazine-2,8-diyl) [PEHIP] and Poly(6,6,12,12-(tetra-2-ethylhexyl)-6,12-dihydrodiindeno[1,2-b:1,2-e]pyrazine-co-2′,3′,6′,7′-tertrakis-octyloxy-9-spirofluorene) [PEHIPSF] were polymerized by using Yamamoto reaction. PEHIP and PEHIPSF showed the PL maximum values of 470 nm and 454 nm in PL spectra. The PEHIPSF was fabricated into an EL device and it exhibited the EL maximum value of 463 nm.

Keywords: blue emitting material; indenopyrazine; OLED; PLED; spirofluorene; Yamamoto polymerization

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INTRODUCTION

Polymer light-emitting diodes (PLEDs) have attracted much attention from academia and industry because of their applications in large area flat-panel displays [1,2]. In particular, interest in PLEDs fabricated from conjugated polymers [3,4] has augmented because such PLEDs have properties that are well-suited to flat panel displays: good processability, low operating voltages, fast response times, and facile color tunability over the full visible range.

On the other hand, a number of issues, such as low electroluminescent (EL) efficiencies and luminescent stability, which need to be resolved, currently spoil their commercial applications, although many light-emitting polymers have been synthesized and investigated, and the performance of PLEDs has been improved greatly in recent years. Therefore, investigation for new conjugated polymers with higher luminescent performance remains one of the major challenges in this area. Among the many kinds of conjugated polymers, PPV and its derivatives are the most extensively investigated polymers employed as emitting layers in PLEDs [5]. But, studies for numerous materials are still continued [6,7].

At the previous study, we synthesized the organic molecules of indenopyrazine derivatives by using a new functional organic material, and the study reported the potential of the synthesized indenopyrazine derivatives as a new OLED core material by applying it as a blue emitting material of OLED [8].

In this paper, we have synthesized new alkylated indenopyrazine homopolymer and its copolymer having an alkylated spirofluorene moiety.

Poly(6,6,12,12-(Tetra-2-ethylhexyl)-6,12-Dihydrodiindeno[1,2-b:1,2-e] pyrazine-2,8-diyl) [PEHIP] and poly(6,6,12,12-(tetra-2-ethylhexyl)-6,12-dihydrodiindeno[1,2-b:1,2-e]pyrazine-co-2′,3′,6′,7′-tertrakis-octyloxy- 9-spirofluorene) [PEHIPSF] were polymerized by using Yamamoto reaction.

Electro-optical properties of these polymers were characterized by cyclic voltammetry (CV), UV-Visible (UV-Vis) and photoluminescence (PL) spectra. Moreover, double-layer EL device was fabricated using PTEDIP and PTEPTOSF as emitting materials.

EXPERIMENTAL

Synthesis

i) Synthesis of 5-Bromo-2,3-dihydro-2-(hydroxyimino) inden-1-one (1)

At a 500 ml round bottom flask, 10 g (47 mmol) of 5-bromo-indanone and 160 ml benzene were added and agitated at room temperature.

After 5 minutes of bubbling with dry HCl gas, the 6.66 g (56 mmol) of amylnitrite was slowly added. While bubbling with dry HCl gas, it was agitated at 40°C for 5 hours. The reactant was additionally agitated for 12 hours at room temperature and the reactant was filtered and washed with methanol (MeOH) and methylene chloride (MC) to acquire pure 5-bromo-2,3-dihydro-2-(hydroxyimino)inden-1-one (1). The yield was 82%.

^{1}H NMR (300 MHz, CDCl3): δ(ppm) 12.72(s, 1H), 7.9(s, 1H), 7.68(s, 2H), 3.78(s, 2H).

ii) Synthesis of 2,8-Dibromo-6,12-dihydrodiindeno [1,2-b:1,2-e]pyrazine (2)

6 g (25 mmol) of synthesized compound (1) was added with 13 g (75 mmol) of sodium dithionite into a 500 ml round bottom flask and 50 ml of ethanol (EtOH) was added. 50 ml of 14.5% ammonia solution was added under the nitrogen atmosphere and agitated at room temperature for 3 days. 50 ml of distilled water was additionally added to the reactant and refluxed. After completing the reaction, 100 ml of distilled water was additionally added after cooling down the reactant and filtered after the agitation, and sufficiently washed with MeOH and diethyl ether before the filtration to acquire 2,8-dibromo-6,12-dihydrodiindeno[1,2-b:1,2-e]pyrazine (2). The yield was 61%.

^{1}H NMR (300 MHz, CDCl3): δ(ppm) 7.96(d, 2H), 7.6(s, 2H), 7.35(d, 2H), 4.06(s, 4H).

iii) Synthesis of 2,8-Dibromo-6,6,12,12-(tetra-2-ethylhexyl)-6,12-dihydrodiindeno[1,2-b:1,2-e]pyrazine (3)

2.0 g (4.83 mmol) of synthesized compound (2) was added with 0.31 g (0.97 mmol) of tetrabutylammonium bromide and 1.62 g (29.0 mmol) of KOH into a 500 ml of round bottom flask, and 24 ml of DMSO was added under the nitrogen atmosphere and agitated at room temperature. After the addition of 5.15 ml (29.0 mmol) of 2-ethylhexyl bromide, the reactant was agitated at room temperature for 48 hours. After completing the reaction, the reactant was extracted with water and ethyl acetate (EA) and dried with $MgSO_4$ before the filtration and washing. The mixture was concentrated and columned by hexane:MC = 20:1 to acquire pure 2,8-dibromo-6,6,12,12-(tetra-2-ethylhexyl)-6,12-dihydrodiindeno[1,2-b:1,2-e]pyrazine (3). The yield was 54%.

^{1}H NMR (500 MHz, CDCl3): δ(ppm) 7.92(d, 2H), 7.62(s, 2H), 7.56(d, 2H), 2.33(m, 4H), 1.93(m, 4H), 1.59(m, 2H), 0.95(m, 58H).

iv) 2,7-Dibromo-2′,3′,6′,7′-tertrakis-octyloxy-9-spirofluoren (4)

Synthetic procedure of 2,7-dibromo-2′,3′,6′,7′-tertrakis-octyloxy-9-spirofluoren (4) was reported in previous paper [9].

^{1}H NMR: d: 7.64(d, 2H), 7.46(m, 2H), 7.19(s, 2H), 6.84(s, 2H), 6.13(s, 2H), 4.10(t, 4H), 3.71(t, 4H), 1.84(m, 4H), 1.34(m, 44H), 0.87(m, 12H).

v) Synthesis of Poly(6,6,12,12-(tetra-2-ethylhexyl)-6,12-dihydrodiindeno[1,2-b:1,2-e]pyrazine-2,8-diyl)(PEHIP)

0.2 g (0.2 mmol) of synthesized compound (3) was used to acquire high molecular weight poly(6,6,12,12-(tetra-2-ethylhexyl)-6,12-dihydrodiindeno[1,2-b:1,2-e]pyrazine-2,8-diyl)(PEHIP) by using the Yamamoto polymerization method [10]. The final yield was 44% (w/w).

vi) Synthesis of Poly(6,6,12,12-(tetra-2-ethylhexyl)-6,12-dihydrodiindeno[1,2-b:1,2-e]pyrazine-co-2′,3′,6′,7′-tertrakis-octyloxy-9-spirofluorene)(PEHIPSF)

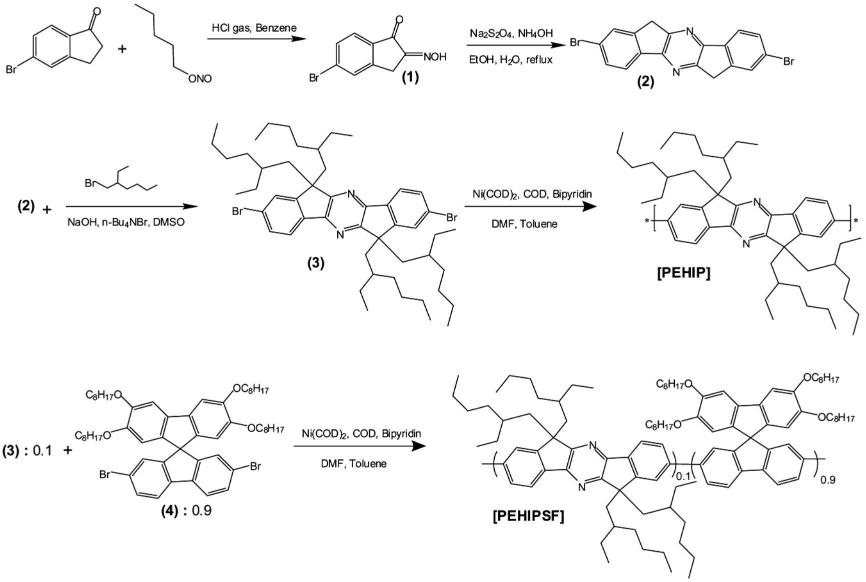
0.3 g of the synthesized compound (3) and compound (4) (mole ratio x:y = 9:1) was used for the Yamamoto polymerization [9] to acquire high molecular weight poly(6,6,12,12-(tetra-2-ethylhexyl)-6,12-dihydrodiindeno[1,2-b:1,2-e]pyrazine-co-2′,3′,6′,7′-tertrakis-octyloxy-9-spirofluorene)(PEHIPSF). The final yield was 82% (w/w).

Characterization

^{1}H-NMR spectra was recorded on a Brucker DPX-300 MHz spectrometer at room temperature. The molecular weights of the polymers were determined by gel permeation chromatography (GPC) analysis using a Waters high pressure GPC assembly Model M410. The optical absorption spectra were measured by a Hewlett Packard 8453 Spectrometer. Perkin Elmer luminescence spectrometer LS50 (Xenon flash tube) was used for photo- and EL spectroscopy. For EL devices, polymer film was prepared by spin coating a solution containing 0.7 wt% of the polymer in toluene. Smooth and pinhole free film with a thickness around 70 nm was easily obtained from the polymer solutions. For double layered device, a modified water dispersion of PEDOT [poly(3,4-ethylenedioxy-thiophene)] doped with poly(styrene sulfonate)(PSS) (Bayer AG, Germany) was used as the hole-injection layer. Cathode (LiF/Al) was deposited with 10^{-6} torr give an emitting area of 9 mm^2. Current-Voltage (I-V) characteristic of the film was measured using Keithley 2400 electrometer. Light intensity was obtained by Minolta CS-100A.

RESULTS AND DISCUSSION

The structures of synthesized polymers are shown in Scheme 1. At the precedent study, we reported the synthesis of new blue emitting



SCHEME 1 Synthetic routes of PEHIP and PEHIPSF.

organic molecules by using indenopyrazine moiety as the new core material and its characteristics [8]. Therefore, this study was designed to characterize the new indenopyrazine polymer system in PLED by firstly applying indenopyrazine unit to polymer backbone.

The number average molecular weights (Mn) of PEHIP and PEHIFSF copolymer were determined by gel-permeation chromatography (GPC) using a polystyrene standard with THF solvent and found to be range from 30,000 to 47,000 g/mol with polydispersity indey of 1.87 and 3.19. PEHIP showed relatively high molecular weight and wider polydispersity of 3.19 as shown in Table 1.

Figure 1 shows the UV-Visible and PL spectra of synthesized PEHIP. Contrary to the 399 nm of UV-Visible absorbance for indenopyrazine monomer, the absorbance of PEHIP was found at 449 nm. PL spectrum also revealed maximum value at 413 nm if it was measured for 6,12-dihydrodiindeno[1,2-b:1,2-e]pyrazine [8], but PEHIP shows the red-shifted PL spectrum at 470 nm and 490 nm. More than 50 nm of red shift could be explained by the longer conjugation length through the polymerization. In addition, the indenopyrazine organic molecule was observed to have very broad PL shape due to the planar chemical structure and its intermolecular interaction. But, in case of PEHIP, the introduction of long alkyl chain reduced the interaction

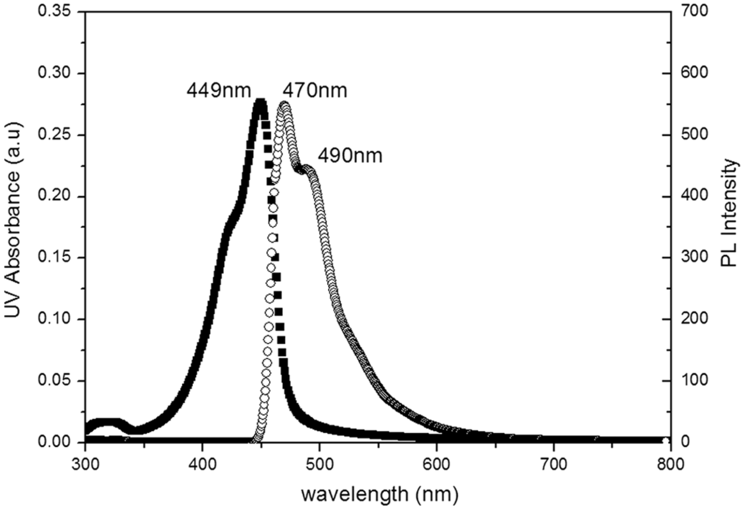


FIGURE 1 UV-visible (■) and PL spectrum (○) of PEHIP films on glass.

between chromophores to enable the clear observation of sharp PL spectrum.

Figure 2 shows the UV-Visible and PL spectra of synthesized PEHIPSF film. For this case, the PL maximum value was observed

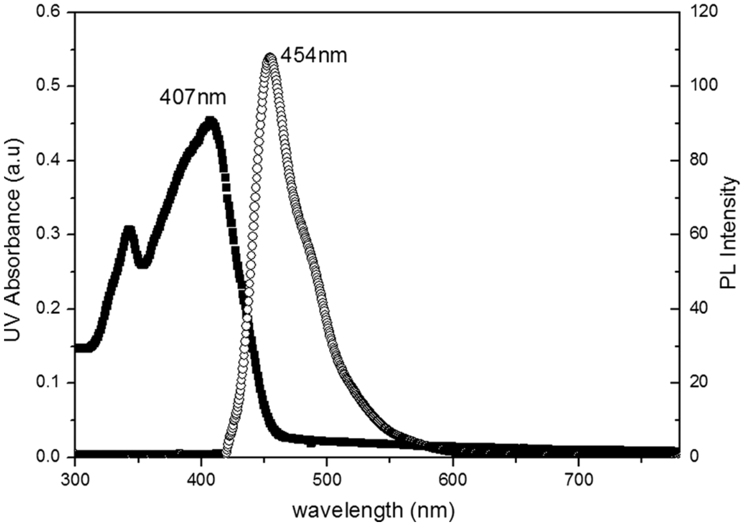


FIGURE 2 UV-visible (■) and PL (○) spectrum of PEHIPSF films on glass.

at 454 nm of deep blue with the maximum absorbance at 407 nm by demonstrating the potential as the wide band-gap and as a blue emitting material. As in the previous case, the introduction of alkyl chain excluded the interaction between chromophores, which enabled to acquire the relatively sharp PL spectrum.

The electrochemical characteristics of the polymers were investigated by using cyclic voltammetric analysis. The first oxidation potential was used to determine the HOMO energy level. Ferrocene was used as an internal standard for calibrating the potential. This data accounts that we could get HOMO level. Based on UV-visible data and CV data, all electronic levels of HOMO, LUMO and band gaps are summarized in Table 1.

The HOMO level of PEHIP and PEHIPSF was found to be 5.31 eV and 5.64 eV, respectively. Since the HOMO level of PEDOT:PSS to be used as the hole injection layer (HIL) is 5.0 eV [10], the applicability of these materials to the HOMO level of HIL material was suitable if these materials are used as the EML. The LUMO level of PEHIP was found to be 2.65 eV that was approximately 0.2 eV elevated compared to the 2.88 eV of PEHIPSF. This could be attributable to the electron withdrawing effect of imine group within the indenopyrazine moiety.

To apply the synthesized polymers in PLED as an emitter, the device was fabricated by the following. The device configuration structure is ITO/PEDOT:PSS (50 nm)/PEHIP or PEHIPSF (70 nm)/LiF (1 nm)/Al(200 nm). The device that used PEHIP as an emitting layer permitted to observe the normal I-V curve and weak luminescence, but revealed quick degradation due to the absence of air stability to electroluminescence, and the acquisition of EL spectrum was not achieved. However, the device that used PEHIPSF allowed to observe the normal EL spectrum at 463 nm even if the efficiency was not so high.

Figure 3 is the EL spectrum that was acquired from the ITO/PEDOT:PSS (50 nm)/PEHIPSF (70 nm)/LiF (1 nm)/Al(200 nm) device. As shown in the figure, a sharp blue luminescence at 463 nm was confirmed. At the precedent our study, we also synthesized the 2′,3′,6′,7′-tertrakis-octyloxy-9-spirofluorene homopolymer (PTOSF) [9] and applied it onto the PLED. As PEHIP, PTOSF also showed very

TABLE 1 Average Molecular Weight, Polydispersity and Thermal Property of PEHIP and PEHIPSF

	Mn	Mw	Poly Dispersity	HOMO	LUMO	Eg
PEHIP	47,000	150,000	3.19	5.31	2.65	2.66
PEHIPSF	30,000	57,000	1.87	5.64	2.88	2.76

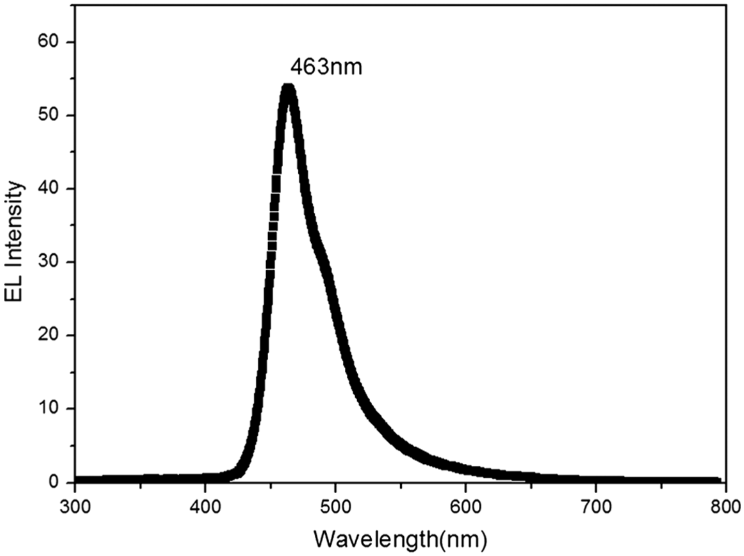


FIGURE 3 EL spectrum of ITO/PEDOT:PSS(50 nm)/PEHIPSF(70 nm)/LiF(1 nm)/Al(200 nm) device at 20 mA/cm^2.

weak luminescence and acquisition of EL spectrum was not achieved. But, the PEHIPSF that were synthesized as a co-polymer form by using the two monomers enabled us to acquire normal EL spectrum at the blue region although it is weak efficiency. It is considered that the cause of the phenomenon could be found from the presence of indenopyrazine unit that withdraws electrons within the molecules to play the role as an electron transporting layer (ETL), which helps the electron supply to spirofluorene unit for the luminescence.

Further studies of synthetic compounds for ETL characteristics are under way.

CONCLUSIONS

Poly(6,6,12,12-(Tetra-2-ethylhexyl)-6,12-Dihydrodiindeno[1,2-b:1,2-e] pyrazine-2,8-diyl) [PEHIP] and Poly(6,6,12,12-(tetra-2-ethylhexyl)-6,12-dihydrodiindeno[1,2-b:1,2-e]pyrazine-co-2′,3′,6′,7′-tertrakis-octyloxy-9-spirofluorene) [PEHIPSF] were polymerized by using Yamamoto reaction. The synthesized PEHIP and PEHIPSF were used to make thin films through the spin-coating and fabricate PLED device as the emitters in order to confirm their luminescence characteristics.

PEHIP and PEHIPSF showed the 470 nm and 454 nm of PL spectrum in blue region, respectively.

PLED device of ITO/PEDOT:PSS (50 nm)/PEHIPSF (70 nm)/LiF (1 nm)/Al(200 nm) showed EL spectrum at 463 nm. Imine group of indenopyrazine having the electron withdrawing effect could be helpful to provide electron to spirofluorene chromophore causing the light.

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