Synthesis and Characterization of Indenofluorene-Based Copolymers Containing 2,5-Bis(2-thienyl)-*N*-arylpyrrole for Bulk Heterojunction Solar Cells and Polymer Light-Emitting Diodes

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ABSTRACT: Two novel alternating π -conjugated copolymers, poly[2,8-(6,6',12,12'-tetraoctyl-6,12-dihydroindeno-[1,2b]fluorenealt-5(1-(2,6-diisopropylphenyl)-2,5-di(2-thienyl)pyrrole) (**P1**) and poly[2,8-(6,6',12,12'-tetraoctyl-6,12-dihydroindeno-[1,2b]fluorenealt-5(1-(p-octylphenyl)-2,5-di(2-thienyl)pyrrole) (**P2**), were synthesized via the Suzuki coupling method and their optoelectronic properties were investigated. The resulting polymers **P1** and **P2** were completely soluble in various common organic solvents and their weight-average molecular weights (M_w) were 5.66 \times 10⁴ (polydispersity: 1.97) and 2.13 \times 10⁴ (polydispersity: 1.54), respectively. Bulk heterojunction (BHJ) solar cells were fabricated in ITO/PEDOT:PSS/polymer:PC₇₀BM(1:5)/TiO_x/Al configurations. The BHJ solar cell with **P1**:PC₇₀BM (1:5) has a power conversion efficiency (PCE) of 1.12% (J_{sc} = 3.39 mA/cm², V_{oc} = 0.67 V, FF = 49.31%), measured using AM 1.5 G solar sim-

INTRODUCTION In recent years, π -conjugated polymers have attracted a great deal of attention because of their possible applications in polymer light-emitting diodes (PLEDs),^{1,2} organic photovoltaics (OPVs),^{3,4} photodetectors,^{4(b)} biosensors,⁵ and field-effect transistors.⁶ For example, polyfluorenes (PFs) and fluorene-based copolymers have been widely studied for their applications especially in PLEDs and/or OPVs because of their large band gap, high photoluminescence (PL) and electroluminescence (EL) efficiencies, and good thermal and chemical stability, and the usual blue light-emitting properties of PFs have generally been tuned by copolymerization with various comonomers.⁷ In polyindinofluorenes (PIFs), the indenofluorene unit has two sites for attaching side alkyl chains and, consequently, better solubility and processability in organic solvents are to be expected. Therefore, PIFs and indenofluorene-based copolymers have been regarded as one of the ideal materials for PLEDs.⁸

Various comonomers have been used for the preparation of indenofluorene-based copolymers in an effort to tune their optical and electrical properties. For example, tetraoctyl and ulator at 100 mW/cm² light illumination. We fabricated polymer light-emitting diodes (PLEDs) in ITO/PEDOT:PSS/emitting polymer:polyethylene glycol (PEG)/Ba/AI configurations. The electro-luminescence (EL) maxima of the fabricated PLEDs varied from 526 nm to 556 nm depending on the ratio of the polymer to PEG. The turn-on voltages of the PLEDs were in the range of 3–8 V depending on the ratio of the polymer to PEG, and the maximum brightness and luminance efficiency were 2103 cd/m² and 0.37 cd/A at 12 V, respectively. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 3169–3177, 2010

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tetra(2-ethylhexyl)indenofluorene, bithiophene, terthiophene, or quaterthiophene were used as comonomers for indenofluorene-based copolymers to control the morphology of the polymer and the optical properties.^{9,10} 9,10-Dibromoanthracene was similarly used as a comonomer for the preparation of an indenofluorene-based copolymer to suppress the aggregate formation of the polymer.¹¹ 4-Hexylbithienopyridine was used as a electron-accepting comonomer for indenofluorene-based copolymers, and the analysis of the microscopic morphology of the thin films of the copolymer by AFM showed a lack of the extensive supramolecular order seen with the homopolymers.¹² Recently, an indenofluorenebased copolymer containing 0.01 mol % 2,1,3-benzothiadiazole (BT) and 0.02 mol % 4,7-bis(2-thienyl)-2,1,3-benzothiadiazole (DBT) was examined for its possible application in white organic light-emitting diodes.¹³ Previously, electron rich 2,5-bis(2-thienyl)-N-dodecylpyrrole has been copolymerized with electron deficient BT and the resulting low band gap π -conjugated oligometric material was applied in bulk heterojunction (BHJ) solar cells.¹⁴ However, 2,5-bis(2-

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thienyl)-*N*-substituted pyrroles have not been used as comonomers for indenofluorene-based copolymers. Although 2,5bis(2-thienyl)-*N*-dodecylpyrrole has been used as a comonomer, 2,5-bis(2-thienyl)-*N*-arylpyrroles have not previously been known. By introducing an *N*-aryl group instead of the *N*-dodecyl group in 2,5-bis(2-thienyl)-*N*-dodecylpyrrole, the molar absorptivity might be improved because the *N*-aryl group increases the π -conjugation length of the molecule. The improved molar absorptivities of 2,5-bis(2-thienyl)-*N*dodecylpyrroles compared with that of 2,5-bis(2-thienyl)-*N*dodecylpyrrole might induce the more effective light absorption and consequently, enhance the power conversion efficiency of the BHJ solar cells fabricated with the copolymers incorporating 2,5-bis(2-thienyl)-*N*-arylpyrroles.

In this study, we wish to report the preparation of two new 2,5-bis(2-thienyl)-*N*-arylpyrroles, the preparation of indenofluorene-based π -conjugated alternating copolymers incorporating 2,5-bis(2-thienyl)-*N*-arylpyrroles and their applications in BHJ solar cells and PLEDs.

EXPERIMENTAL

Materials and Instruments

All reagents were purchased from Aldrich (St. Louis, MO, USA) or TCI chemicals (Tokyo, Japan) and used without further purification. Solvents were purified by the standard procedure and handled in a moisture-free atmosphere. Flash column chromatography was performed using silica gel (Merck Kieselgel 60, 70-230 mesh). ¹H and ¹³C NMR spectra were recorded on a Varian Mercury Plus 300 spectrometer and the chemical shifts were recorded in ppm units with chloroform as the internal standard. The UV-visible and emission spectra were recorded with JASCO V-570 and Hitachi F-4500 fluorescence spectrophotometers, respectively. The solid state emission measurements were carried out by supporting each film on a quartz substrate, which was mounted so as to receive the front-face excitation at an angle of less than 45 °. Each polymer film was excited with several portions of the visible light from a xenon lamp. The molecular weight and polydispersity of the polymer were determined by gel permeation chromatography (GPC) using a PLgel 5 µm MIXED-C column on an Agilent 1100 series liquid chromatography system with THF as an eluent and with a polystyrene standard calibration. The thermal analyses were performed on a Mettler Toledo TGA/SDTA 851, DSC 822 analyzer under an N₂ atmosphere at a heating rate of 10 °C/min. Cyclic voltammetry (CV) was performed on a CH Instruments Electrochemical Analyzer. The measurements were carried out in chloroform solutions containing 0.1 M tetrabutylammonium tetrafluoroborate (Bu₄NBF₄) as the supporting electrolyte, using Ag/AgCl as a reference electrode, a platinum wire as a counter electrode and an internal ferrocene/ferrocenium (FOC) standard.

Device Preparation

The BHJ solar cells used to measure the photovoltaic properties were constructed as follows. Each glass substrate was coated with a transparent ITO electrode (110 nm thick, 20 Ω /sq sheet resistance). The ITO-coated glass substrates were ultrasonically cleaned successively with detergent, deionized water, acetone, and isopropyl alcohol. A 40 nm thick layer of PEDOT:PSS (H.C.Stack, PH500) was spin-coated onto the precleaned and UV-ozone treated ITO substrates. The spin-coated film was baked in air at 150 °C for 30 min. For the fabrication of the active layers composed of interconnected networks of the electron donor and acceptor, 1,2dichlorobenzene and chloroform (1:1 wt %) solutions of the synthesized polymer (10 mg/mL) and 1-(3-methoxycarbonyl)propyl-1-phenyl[6,6]C₇₀ (PC₇₀BM) (20 mg/mL) were shaken at room temperature for 12 h. The polymer and PC70BM blends were then prepared by mixing the two solutions and subsequently shaking them for 12 h. Filtration using a 0.45 μ m PTFE (hydrophobic) syringe filter gave the polymer blends with a ratio of the electron donor to PC70BM as the electron acceptor of 1:5 wt %, respectively. The TiO_x precursor solution (1 wt %) was spin-cast (4000 rpm) onto the active layer with a thickness of about 10 nm and heated at 80 °C for 10 min in air. After being subjected to a vacuum $(5 \times 10^{-6} \text{ Torr})$, the Al electrodes with a thickness of around 100 nm were deposited. The device was then subjected to annealing at 100 °C for 30 min. The top metal electrode area, comprising the active area of the solar cells, was found to be 4 mm². The performance of the BHJ solar cells were measured using a AM 1.5 G solar simulator (Oriel 300 W) at 100 mW/cm² light illumination after adjusting the light intensity using an Oriel power meter (model No. 70,260 ,which was calibrated using laboratory standards that are traceable to the National Institute of Standards and Technologies). The current density-voltage (I-V) curves were recorded using a standard source measurement unit (Keithley 236). All fabrication steps and characterization measurements were performed in an ambient environment without a protective atmosphere. The thickness of the thin films was measured using a KLA Tencor Alpha-step IQ surface profilometer with an accuracy of ± 1 nm.

The PLEDs were fabricated on the ITO-coated glass substrates (80 nm thick, 20 Ω /sq sheet resistance). The substrates were ultrasonically cleaned successively with detergent, deionized water, acetone, and isopropyl alcohol. A 40nm thick layer of PEDOT:PSS (H.C. Stack, AI 4083) was spincoated onto the precleaned and UV-ozone treated ITO substrates. Then, the spin-coated film was baked in air at 150 °C for 20 min. The polymer and PEG solution was prepared in 1,2-dichlorobenzene solvent at weight concentrations of 20 mg/ml and 10 mg/ml, respectively. All the solutions used in the fabrication of the PLEDs were filtered with a 0.45 μ m PTFE (hydrophobic) syringe filter. These solutions were then mixed at various ratios to give appropriate weight percentages and spin coated on top of the PEDOT:PSS layer to obtain an emitting layer thickness of 80-100 nm. The emitting layer was then annealed at 80 °C for 30 min. In order to investigate the effect of poly(ethylene glycol) (PEG) on the performance of the PLEDs, we fabricated with various concentrations (0 wt %, 5 wt %, and 10 wt %) of PEG. The film thickness was measured with an α -Step IQ surface profiler (KLA Tencor, San Jose, CA). Ba and Al metals were deposited



SCHEME 1 Synthetic route of dibrominated monomers **3** and **5**

on top of each polymer film through a mask by vacuum evaporation at a pressure of less than 5×10^{-6} Torr, yielding an active area of 4 mm². To characterize the device, the current density-voltage-luminescence (*J-V-L*) changes were measured using a current/voltage source meter (Keithley 236) and an optical power meter (CS-1000). All the processes and measurements mentioned above were carried out in the open air at room temperature.

Synthesis

The monomers and polymers were synthesized as shown in Schemes 1 and 2, respectively. The detailed synthetic procedures are as follows.

1-(2,6-Diisopropylphenyl)-2,5-di(2-thienyl)pyrrole (2)

1,4-Bis(2-thienyl)-1,4-butanedione (1) (5.0g, 20mmol), which was prepared via the previously reported procedure,¹⁵ and 2,6-diisopropylaniline (15.2 mL, 80mmol) were dissolved in 40 mL of a toluene-acetic acid (3:1) mixture. The mixture was refluxed with a dean stark condenser for 72 h under nitrogen, cooled to room temperature and then 100 mL of toluene was added to this mixture. The insoluble material was filtered off. The obtained toluene solution was concentrated in vacuo and then poured into a saturated Na₂CO₃ solution to make the reaction mixture basic. The organic layer was separated and then the aqueous layer was extracted with toluene (50 mL \times 3). The combined organic layers were washed with water, dried over anhydrous Na₂SO₄ and then concentrated in vacuo. The residue was purified by column chromatography (silica gel, toluene) and then recrystallized from acetone to afford the pure product. Yield: 4.5g (58%). mp 106–107 °C; ¹H NMR (300 MHz, CDCl₃) δ (ppm) 7.54-7.58 (t, 1 H), 7.26-7.30 (dd, 2 H), 6.97-6.99 (dd, 2 H), 6.76-6.79 (dd, 2H), 6.68 (s, 2H), 6.40-6.42 (dd, 2H) 2.47-2.57 (m, 2 H), 0.89-0.92 (d, 12 H); ¹³C NMR (75 MHz, CDCl₃): δ (ppm) 148.29, 135.40, 134.46, 130.52, 130.30, 127.13, 124.82, 123.34, 123.03, 109.28, 28.53, 23.90; HRMS $(EI^+, m/z)$ $[M^+]$ Calcd for $C_{24}H_{25}NS_2$ 391.1428, found 391.1426; Anal. Calcd for C24H25NS2: C, 73.61; H, 6.43; N, 3.58; S, 16.38. Found: C, 73.12; H, 6.59; N, 3.63; S, 16.76.

1-(2,6-Diisopropylphenyl)-2,5-di(2-thienyl-5-bromo)pyrrole (3)

1-(2,6-Diisopropylphenyl)-2,5-di(2-thienyl)pyrrole (2) (3.0 g, 7.7 mmol) was dissolved in 30 mL of DMF. The solution was cooled with an ice bath and then NBS (2.8 g, 15.7 mmol) in

10 mL of DMF was added dropwise to the solution at 0 °C. The solution was stirred for 5 h. The solvent was concentrated in vacuo and the solid was dissolved in 50 mL of CHCl_{3.} The organic solution was washed well with water and brine solution and dried over anhydrous Na₂SO₄. The solvent was removed and the residue was purified by flash column chromatography (silica gel, hexane) to afford the pure product. Yield: 3.8 g (90%). mp 195-196 °C; ¹H NMR (300 MHz, CDCl₃): δ (ppm) 7.53–7.59 (t, 1H), 7.28–7.30 (d, 2 H), 6.70– 6.72 (d, 2 H), 6.59 (s, 2H), 6.25-6.45 (d,2H), 2.36-2.46 (m, 2 H), 0.89–0.92 (d, 12 H); ¹³C NMR (75 MHz, CDCl₃): δ (ppm) 148.09, 136.70, 133.61, 131.11, 130.02, 129.73, 125.16, 123.07, 110.13, 109.47, 28.51, 23.97; HRMS (EI⁺, m/z) [M⁺] Calcd for C24H23Br2NS2 546.9639, found 546.9641; Anal. Calcd for C₂₄H₂₃Br₂NS₂: C, 52.47; H, 4.22; Br, 29.09; N, 2.55; S, 11.67. Found: C, 52.56; H, 4.38; N, 2.29; S, 11.24.

1-(p-Octylphenyl)-2,5-di(2-thienyl)pyrrole (4)

1-(p-Octylphenyl)-2,5-di(2-thienyl)pyrrole (4) was synthesized by the same procedure as that for 1-(2,6-diisopropylphenyl)-2,5-di(2-thienyl)pyrrole (2) except for the use of *p*-octylaniline instead of 2,6-diisopropylaniline. Yield: 6.3g (55%). mp 110–111 °C; ¹H NMR (300 MHz, CDCl₃): δ (ppm) 7.25 (s, 4 H), 7.02–705 (dd, 2 H), 6.79–6.83 (m, 2 H), 6.50– 6.55 (m, 4H), 2.67–2.72 (t, 2 H), 1.64–1.70 (m, 2 H), 1.29– 1.33 (m, 10 H), 0.88–0.92 (t, 3 H). ¹³C NMR (75 MHz, CDCl₃); δ (ppm) 144.50, 136.11, 135.35, 130.43, 129.93, 129.42, 127.07, 124.20, 124.01, 109.75, 35.87, 32.10, 31.48, 29.68, 29.55, 29.33, 22.93, 14.37; HRMS (EI⁺, m/z) [M⁺] Calcd for C₂₆H₂₉NS₂ 419.1741, found 419.1740; Anal. Calcd for C₂₆H₂₉NS₂: C, 74.41; H, 6.97; N, 3.34; S, 15.28. Found: C, 74.55; H, 7.00; N, 3.27; S, 15.44.

1-(p-Octylphenyl)-2,5-di(2-thienyl-5-bromo)pyrrole (5)

1-(p-Octylphenyl)-2,5-di(2-thienyl-5-bromo)pyrrole (**5**) was synthesized by the same procedure as that for 1-(2,6-diiso-propylphenyl)-2,5-di(2-thienyl-5-bromo)pyrrole (**3**). Yield: 0.6 g (15%). mp 100–101 °C; ¹H NMR (300 MHz, CDCl₃): δ (ppm) 7.24–7.26 (d, 2H), 7.17–7.19 (d, 2 H), 6.74–6.76 (d, 2 H), 6.47 (s, 2H), 6.31–6.33 (d, 2 H), 2.67–2.72 (t, 2 H), 1.64–1.70 (m, 2 H), 1.29–1.33 (m, 10 H), 0.88–0.92 (t, 3 H); ¹³C NMR (75 MHz, CDCl₃): δ (ppm) 145.06, 136.56, 135.27, 129.98, 129.93, 129.79, 124.47, 110.88, 109.91, 35.84, 32.13, 31.34, 29.69, 29.52, 29.23, 22.92, 14.36. HRMS (EI⁺, m/z) [m⁺] Calcd for C₂₆H₂₇Br₂NS₂ 574.9952, found 574.9956;



Anal. Calcd for C₂₆H₂₇Br₂NS₂: C, 54.08; H, 4.71; Br, 27.68; N, 2.43; S, 11.11. Found: C, 53.80; H, 4.55; N, 2.32; S, 10.70.

General Procedure for Polymerization

The alternating copolymers P1 and P2 were synthesized by the Suzuki coupling reaction of monomer 6, which was prepared via a known procedure, 12,13 with monomers **3** and **5**, respectively, and then end-capped with bromobenzene and phenylboronic acid as shown in Scheme 2. A solution of the monomers 6 (0.24 g, 0.25 mmol) and 3 (0.14 g, 0.25 mmol) for polymer P1 or the monomers 6 (0.24 g, 0.25 mmol) and 5 (0.14 g, 0.25 mmol) for polymer P2 and Pd $(PPh_3)_4$ (0.02 g, 4 mol %) in dry THF (60 mL) was purged well with nitrogen for 45 min. To the solution was added aqueous 2 M K_2CO_3 (6 mL). The whole solution was refluxed with vigorous stirring for 36 h under nitrogen. To the reaction mixture 30 mg of phenylboronic acid was added. The whole mixture was refluxed for 6 h and then 0.03 mL of bromobenzene was added and refluxed again for 6 h. The reaction mixture was cooled and then poured into methanol (200 mL) with vigorous stirring. The precipitate was recovered by filtration, washed with dilute HCl solution and then extracted with methanol for 12 h and acetone for 24 h in a Soxhlet apparatus. The residue was then dissolved twice in chloroform and reprecipitated from methanol to give the polymer as an orange colored solid. Polymer P1: Yield (0.2 g, 67%). ¹H NMR (300 MHz, CDCl₃): δ 7.36–7.67 (m, 11H), 7.03–7.04 (d, 2H), 6.77 (s, 2H), 6.13-6.14 (d, 2H), 2.63 (m, 2H), 2.00 (s, 8H), 1.04 (m, 50H), 0.77 (t, 12H), 0.66 (s, 8H); ¹³C NMR (75 MHz, CDCl₃): δ (ppm) 152.06, 150.61, 148.13, 142.23, 141.01, 140.36, 135.00, 13,451, 132.82, 130.36, 124.93, 124.45, 123.16, 123.07, 120.02, 119.92, 114.05, 109.78, 54.96, 40.78, 32.01, 30.22, 29.96, 29.41, 24.67, 23.99, 22.80, 14.27; Anal.

SCHEME 2 Synthetic route of polymers P1 and P2

Calcd for $C_{76}H_{101}NS_2$: C, 83.53; H, 9.32; N, 1.28; S, 5.87. Found: C, 79.04; H, 9.10; N, 1.14; S, 5.34. Polymer **P2**: Yield (0.21 g, 70%). ¹H NMR (300 MHz, CDCl₃): δ 7.28–7.67 (m, 12H), 7.09–7.10 (d, 2H), 6.64 (s, 2H), 6.39–6.40 (d, 2H), 2.75 (t, 2H), 2.00 (s, 8H), 1.74 (s, 2H), 1.57 (s, 2H), 1.04 (s, 48H), 0.77 (s, 15H), 0.66 (s, 8H); ¹³C NMR (75 MHz, CDCl₃): δ (ppm) 152.05, 150.57, 144.65, 143.15, 141.06, 140.42, 134.34, 132.89, 130.70, 129.97, 129.64, 124.80, 124.49, 123.02, 119.93, 119.71, 114.92, 110.09, 55.00, 40.86, 35.95, 32.15, 32.00, 31.70, 30.21, 29.92, 29.71, 29.39, 23.94, 22.91, 22.78, 14.35, 14.24. Anal. Calcd for $C_{78}H_{105}NS_2$: C, 83.59; H, 9.44; N, 1.25; S, 5.72. Found: C, 80.35; H, 9.83; N, 1.02; S, 4.73.

RESULTS AND DISCUSSION

Polymer Synthesis and Characterization

2,5-Bis(2-thienyl)-N-(2,6-diisopropylphenyl)pyrrole (2) and 2,5-bis(2-thienyl)-N-(4-octylphenyl)pyrrole (4) were prepared by simply treating 1,4-bis(2-thienyl)-1,4-butanedione (1) with 2,6-diisopropylamine or 4-octylamine in the presence of acetic acid in toluene, as shown in Scheme 1. We found that the molar absorptivities of compounds 2 and 4 were greater than that of 2,5-bis(2-thienyl)-*N*-dodecylpyrrole and the UV absorption maxima of compounds 2 and 4 were red-shifted compared to that of 2,5-bis(2-thienyl)-N-dodecylpyrrole, as shown in Figure 1. The greater molar absorptivities of compounds 2 and 4 compared to that of 2,5-bis(2thienyl)-N-dodecylpyrrole might induce the more effective light absorption and consequently, the power conversion efficiency of the BHJ solar cells fabricated with the copolymer incorporating compound 2 or compound 4 might be improved.



FIGURE 1 UV-Visible absorption spectra of (A) 2,5-bis(2-thienyl)-*N*-dodecylpyrrole, (B) 2,5-bis(2-thienyl)-*N*-(4-octylphenyl)pyrrole, and (C) 2,5-bis(2-thienyl)-*N*-(2,6-diisopropylphenyl)-pyrrole in chloroform $(1 \times 10^{-5} \text{ M})$ solution.

Compounds 2 and 4 were brominated with NBS to afford brominated monomers 3 and 5, respectively, as shown in Scheme 1. Then, the Suzuki polymerization between the diboronic ester of indinofluorene 6 and brominated monomer 3 or 5 was carried out to afford polymers P1 and P2, as shown in Scheme 2. The chemical structures of the monomers and polymers prepared in this study were verified by NMR and elemental analysis. Both polymers P1 and P2 exhibited very good solubility in common organic solvents such as chloroform, chlorobenzene, dichlorobenzene, tetrahydrofuran, and toluene. The weight average molecular weights (M_w) of polymers P1 and P2 were found to be 56,600 and 21,300 and their polydispersities were 1.98 and 1.54, respectively. Both polymers showed high thermal stability, with 5%

TABLE 1 Polymerization Results, Thermal and Electro-opticalProperties of Polymers P1 and P2

		P1	P2
$M_{ m w} imes$ 10 ^{4a}		5.66	2.13
PDI ^a		1.97	1.54
TGA ^b		430	370
Abs (nm)	Solution	465	440
	Film ^c	465	440
PL (nm)	Solution	530	515
	Film ^c	551, 522, 600	524, 560
Φ_{PL} (%) ^d		41	19
E _g ^e (eV)		2.36	2.40

^a Weight average molecular weight (M_w) and polydispersity (PDI) of the polymers were determined by GPC using polystyrene standards.

 $^{\rm b}$ Onset decomposition temperature (5 % weight loss) measured by TGA under $N_2.$

 $^{\rm c}$ Measurements in thin film were performed onto the quartz substrate. $^{\rm d}$ Estimated by using a THF solution of ${\sim}10^{-3}$ M of 9,10-diphenylanthra-

cene in PMMA as a standard (90 %).

^e Band gap estimated from the onset wavelength of the optical absorption in thin film.

weight loss occurring at 430 °C and 370 °C, respectively (see Supporting Information, Figure S1). The polymerization results and thermal properties of polymers P1 and P2 are summarized in Table 1.

Optical and Electrochemical Properties

The optical and PL properties of polymers P1 and P2 were measured both in chloroform solution and in the form of a thin film. Figure 2 shows the solution and thin film state absorption spectra of the polymers. The absorption maxima of polymers P1 and P2 were 465 nm and 440 nm, respectively, in both solution and thin film states. The absorption maximum of polymer P1 is red-shifted by 25 nm compared with that of polymer P2, because of the presence of the sterically hindered isopropyl groups in the N-phenyl ring. The sterically hindered isopropyl groups in the phenyl ring of polymer P1 restrict the rotation of the C-N bond and, consequently, the π -conjugation length of polymer **P1** is increased compared to that of polymer P2. The optical band gaps of polymers P1 and P2 were calculated from the onset wavelength of the optical absorption in solution to be 2.36 and 2.40 eV, respectively.

Figure 3 shows the PL spectra of polymers **P1** and **P2**. The PL measurements were carried out in chloroform and in the thin film state on photo excitation at 465 nm and 440 nm, respectively. Polymers **P1** and **P2** exhibited green emission peaks at around 530 nm and 515 nm, respectively, in solution. The PL spectra of the polymers **P1** and **P2** in the thin film state are somewhat red-shifted compared to those in solution and some shoulder peaks are observed in the spectra of both polymers. The shoulder peaks are due to the presence of an additional band that can be superimposed on the mutual PL band, which was observed as a more pronounced second vibronic band. This additional band feature might be due to the increased intermolecular interaction of the π -conjugated polymer backbones.¹⁶ Polymer **P1** shows a maximum PL emission at 551 nm with two shoulder peaks at



FIGURE 2 UV-visible absorption spectra of polymers P1 and P2 in chloroform and thin film.

522 nm and 600 nm, and polymer **P2** shows a maximum PL emission at 524 nm with a shoulder peak at 560 nm. The PL efficiencies of **P1** and **P2** in solution were measured by comparison with 9,10-diphenylanthracene as the standard. The PL quantum efficiencies of **P1** and **P2** are 41 % and 19 %, respectively, and their electro-optical data are summarized in Table 1. The high PL efficiency of **P1** is due to the sterically hindered isopropyl group in the phenyl ring of **P1**, which inhibits the intermolecular interaction between the polymer backbones.

The electrochemical behaviors and electrochemical stabilities of polymers **P1** and **P2** were investigated by CV. From the CV measurements, the HOMO energy levels of polymers **P1** and **P2** were calculated to be -5.19 eV and -5.20 eV, respectively (see Supporting Information, Figure S2).

The LUMO energy levels were calculated from the values of the band gaps and HOMO energies. The LUMO energy levels of polymers P1 and P2 were calculated to be -2.83 eV and -2.80 eV, respectively. The energy band diagram of polymers P1 and P2 and PC₇₀BM is illustrated in Figure 4. In general, the electron transfer takes place from the high energy level to the low energy level and the hole transfer takes place from the low energy level to the high energy level. In BHJ solar cells, the incident light causes electron to be ejected from the HOMO energy level of the π -conjugated polymer to its own LUMO energy level, and then the excited electron moves to the next lower energy level, i.e., the LUMO of $PC_{70}BM$. If the LUMO of PC₇₀BM is higher than that of the π -conjugate polymer, the electron movement is not possible. Efficient electron transfer occurs only when the LUMO level of $PC_{70}BM$ is located below the LUMO of the π -conjugated polymer.

The LUMO level of $PC_{70}BM$ is -4.3 eV,¹⁷ which is below the LUMO level of polymers **P1** and **P2**. These results indicate that polymers **P1** or **P2** can be used as electron donors in BHJ solar cells.



FIGURE 3 Photoluminescence spectra of polymers P1 and P2 in chloroform and thin film.



FIGURE 4 The energy level diagram of polymers P1 and P2 and PC₇₀BM with all other materials used in BHJ solar cell.

BHJ Solar Cell Properties

BHJ solar cells were fabricated using polymers P1 or P2 as the electron donor and $PC_{70}BM$ as the electron acceptor. The structure of BHJ solar cells was as follows: ITO/PEDOT:PSS/ Polymer:PC₇₀BM (1:5)/TiO_x (10 nm)/Al (100 nm). We also used solution processable TiO_x between the active layer and the metal cathode as a hole blocking and electron transporting layer. 18,19 The energy level of $\mathrm{TiO}_{\mathrm{x}}$ matches the workfunction of Al well. Many research groups have obtained excellent photovoltaic performances through the optimization of the ratio of the electron donor polymers to the electron acceptor PC70BM.20 The charge balance generally depends on the thickness of the active layer and the amount of PC₇₀BM in the polymer blended active layer. In this study, we probed the effect of the ratio of polymers P1 or P2 to PC₇₀BM on the photovoltaic performance using a mixed solvent system consisting of 1,2-dichlorobenzene and chloroform. The best blending ratio of polymers P1 or P2 to PCBM was 1:5, which gave the optimal photovoltaic performances of the BHJ solar cells. The current density-voltage (J-V)



FIGURE 5 I-V characteristics of BHJ solar cells prepared from ITO/PEDOT:PSS/P1:PC₇₀BM (1:5)/TiOx/AI (a), ITO/PEDOT:PSS/P2:PC₇₀BM (1:5)/TiOx/AI and (b) under AM 1.5 irradiation (100 mW/cm²).

TABLE 2 Solar Cell Performance of Polymers **P1** and **P2** asElectron Donor with $PC_{70}BM$ as an Electron Acceptor in ITO/PEDOT:PSS/Polymer:PC_{70}BM /TiO_x/AI Device

Polymer	$V_{\rm oc}~({\rm V})^{\rm a}$	J _{sc} (mA/cm ²) ^b	FF (%) ^c	PCE (%)
P1	0.67	3.39	49.31	1.12
P2	0.57	1.26	32.02	0.23

^a Open-circuit voltage.

^b Short-circuit current density.

 $^{\rm c}$ Fill factor.

^d Power conversion efficiency.

characteristics of ITO/PEDOT:PSS/**P1**:PC₇₀BM (1:5)/TiO_x/Al [(a) **P1** device] and ITO/PEDOT:PSS/**P2**:PC₇₀BM (1:5)/TiO_x/Al [(b) **P2** device] fabricated with a 1:5 ratio of polymers **P1** or **P2** to PC₇₀BM, under AM 1.5G illumination, are shown in Figure 5 and summarized in Table 2.

The **P1** device performance shows an open circuit voltages (V_{oc}) of 0.67 V, short-circuit current density (J_{sc}) of 3.39 mA/ cm², fill factor (FF) of 49.31 %, and conversion efficiency (PCE) of about 1.12 %, whereas the **P2** device exhibits a lower V_{oc} (0.57 V), J_{sc} (1.26 mA cm⁻²⁾ and FF (32.02 %) than the **P1** device, leading to a lower PCE of 0.23 %. The PCEs of polymers **P1** and **P2** were lower than that of poly(3-hex-



FIGURE 6 Current density-voltage-luminance-efficiency (*I-V-L-η*) characteristic of the ITO/PEDOT/polymer **P1**:PEG/Ba/Al device.



FIGURE 7 Current density-voltage-luminance-efficiency (*I-V-L-\eta*) characteristic of the ITO/PEDOT/polymer **P2**:PEG/Ba/Al device.

ylthiophene) (P3HT), although all of the properties of polymers **P1** and **P2** are similar to those of P3HT. The main reason for the low photovoltaic performance was the lower short-circuit current density and fill factor. The optimization of the BHJ solar cells is currently in progress.

PLED Properties

PLEDs based on polymers P1 and P2 were fabricated with configuration ITO/PEDOT/polymer:PEG/Ba/Al. The the blended emission layer was then deposited by spin coating using a solution containing polymer P1 or P2 and PEG in 1,2-dichlorobenzene in an appropriate weight proportion. Recently, it was reported that the performance of PLEDs can be substantially improved by introducing a thin layer of a polymer oxide such as PEG or poly(ethylene oxide) (PEO) on the cathode interface or by blending such materials into the emission layer of the PLEDs.²¹ We expected that the presence of PEG in the emission layer would reduce the contact resistance and electron injection barrier between the active layer and cathode, thereby lowering the operating voltage. Also, Deng et al. reported that the improvement in efficiency was due to the improved electron injection at the interface, which was the result of the specific interfacial interactions

Polymer: % PEG	Turn-on (V) ^a	Voltage (V) ^b	L _{max} (cd/m ²) ^c	LE _{max} (cd/A) ^d	EL (nm) ^e
		-			
P1 : 0 % PEG	8	12	53.14	0.017	556
P1 : 5 % PEG	5	10	278	0.064	548
P1 : 10 % PEG	3	12	2103	0.37	526
P2 : 0 % PEG	6.5	12	36.15	0.014	549
P2 : 5 % PEG	6	12	250.1	0.069	536
P2 : 10 % PEG	4.5	12	702.3	0.16	532

TABLE 3 PLED Performances of Devices Fabricated With Polymers P1 and P2 Blended With and Without PEG

 $^{\rm a}$ Voltage required to achieve a brightness of 1 cd/m $^{\rm 2}.$

^b Measured under the condition of maximum brightness.

^c Maximum luminescence.

between PEG and the cathode.²² In order to determine the optimum weight ratio of polymer P1 or P2 to PEG, the performances of the PLEDs with different weight ratios of polymer P1 or P2 to PEG were compared. The device characteristics of the PLEDs fabricated with different weight ratios of PEG, viz. 0 wt %, 5 wt %, and 10 wt %, were measured. Figures 6 and 7 show the current density-voltage-luminance-efficiency (*I-V-L-* η) characteristics of polymers **P1** and **P2** with different compositions of PEG in the emission layer. The turn-on voltage and maximum brightness of polymer P1 without PEG in the emitting layer were 8 V and 53 cd/m^2 at 12 V, respectively. By blending PEG into the polymers P1 and P2, the PLED performance was significantly enhanced. To investigate the effect of PEG on the performance of PLEDs, we fabricated PLEDs with 5 wt % and 10 wt % of PEG. The turn-on voltages of polymer P1 with 5 wt % and 10 wt % of PEG were 5 V and 3 V and their maximum brightnesses were 278 cd/m^2 and 2,103 cd/m^2 , respectively. Increasing the amount of PEG in the emitting layer to more than 10 wt % did not result in any further improvement in the PLED performance. The PLED performance of polymer



FIGURE 8 EL spectra of the ITO/PEDOT/polymer P1 and P2/Ba/ Al devices.

^d Maximum luminescence efficiency.

^e Maximum of EL spectrum.

P2 was investigated in a similar fashion. The maximum brightness and current efficiency of polymer **P2** were 702 cd/m^2 at 12 V and 0.16 cd/A, respectively. Table 3 summarizes the PLED performance of the devices fabricated with polymers **P1** and **P2** blended with and without PEG.

Figure 8 shows the EL spectra of polymers **P1** and **P2**. The EL spectra of polymers **P1** and **P2** were almost identical to the PL spectra shown in Figure 3. The maximum EL peak of polymer **P1** was observed at 556 nm without PEG. This maximum EL peak is red-shifted by 30 nm compared to that of the polymer with 10 wt % PEG (526 nm). The device with 5 wt % PEG shows a maximum EL peak at 548 nm (see Supporting Information, Figure S3). The addition of PEG leads to an increase of the luminance efficiency and, at the same time, leads to the blue shift of the maximum EL peak.

CONCLUSIONS

This study focused on the molecular design of heteroaromatic monomers and the synthesis of new indenofluorenebased alternating copolymers for BHJ solar cell and PLED applications. Their potential applications in BHJ solar cells and PLEDs are discussed. Good solubility in common organic solvents, thermal stability, reasonable photovoltaic performance, and efficient green emission were demonstrated with our developed polymers, P1 and P2. BHJ solar cells with the configuration ITO/PEDOT/polymer:PC₇₀BM (1:5)/TiO_x/Al were fabricated with polymers P1 and P2 as the electron donors and PC70BM as the electron acceptor. For the BHJ solar cells based on polymer P1:PC70BM (1:5), the maximum $V_{\rm oc}$, $J_{\rm sc}$, and FF values reached 0.67 V, 3.39 mA/cm², and 49.31 %, respectively, and the PCE was 1.12 %. The PLEDs (PLED architecture:ITO/PEDOT/polymer:PEG/Ba/Al) based on polymers P1 and P2 showed a green emission at about 550 nm with a maximum brightness, current efficiency and turn-on voltage of 2,103 cd/m², 0.37 cd/A and 3.0 V, respectively. This indicates that P1 and P2 are promising polymers for the development of optoelectronic devices such as BHJ solar cells and PLEDs.

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