

Highly Soluble Fluorenyl-Substituted Poly(1,4-phenylenevinylene) for Bright and Efficient Blue–Green Light-Emitting Diode

Sang Ho Lee,^{*,†} Bo-Bin Jang,[†] and Tetsuo Tsutsui^{†,‡}

[†]CREST, Japan Science and Technology Corporation (JST)

^{‡‡}Department of Applied Science for Electronics and Materials, Graduate School of Engineering Science, Kyushu University, Kasuga, Fukuoka 816-8580

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Poly[2-(9',9'-dihexylfluorenyl)-1,4-phenylenevinylene] (DHF-PPV), which contains 9,9-dihexylfluorene as a pendant group, was synthesized by the modified Gilch polymerization of the corresponding bischloromethyl-substituted benzene monomer. Light emitting device fabricated with DHF-PPV showed high electroluminescence efficiency with low turn-on voltage.

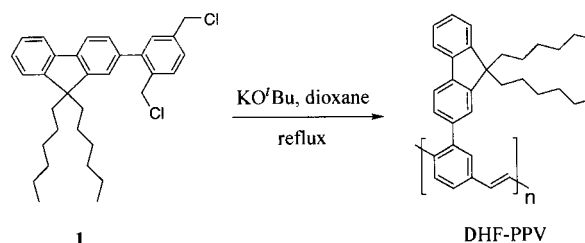
Conjugated polymers with delocalized π -electron bonding along polymer chains offer opportunities for a number of applications as active materials, such as light-emitting diodes,¹ light-emitting electrochemical cells,² photovoltaic diodes,³ photodetectors,⁴ solid-state lasers,⁵ and biological and chemical sensors.⁶ Among these applications, considerable progress has been achieved in polymer light-emitting diodes (PLEDs) during the past ten years. Fully conjugated polymer, PPV, is insoluble, intractable, and infusible. So, most of investigations of PPVs have focused on PPV derivatives with 2-substituted and/or 2,5-disubstituted alkoxy groups on the aromatic rings because of their easy synthesis and high solubility. Another major object for introducing alkoxy groups to the PPV chain would be the improvement of photoluminescence (PL) efficiency. For example, the branched side chain-containing MEH-PPV⁷ could obtain a quite respectable efficiency of 1.0% with a simple electroluminescence device of ITO/MEH-PPV/Ca. This can be reasonably accepted from the fact that the close packing between the conjugated polymer backbones, which leads to a self-quenching process of excitons, is prevented by long side chains.

Some research groups have introduced phenyl groups to the PPV backbone,⁸ or synthesized steric hindered 2,3-disubstituted PPV⁹ as a tool for increasing PL efficiency of PPVs. These polymers have common characteristic of the distortion of intra- and intermolecular chain interactions as a result of steric effects. Recently, it has been reported that soluble phenyl-substituted PPVs exhibit highly efficient brightness and excellent power efficiency.^{8b}

Here we report that the introduction of dialkylfluorenyl groups to the PPV backbone is quite effective for the increase of emission efficiency of PLEDs with maintaining high processability. We stress the fact that a simple PPV homopolymer exhibits high LED performance.

Poly[2-(9',9'-dihexylfluorenyl)-1,4-phenylenevinylene] (DHF-PPV) was synthesized by the modified Gilch procedure¹⁰ (dehydrohalogenation polymerization) of the corresponding bischloromethyl-substituted benzene monomer (**1**)¹¹ (Scheme 1). The polymer dissolved in hot THF (60 °C) was purified by precipitation from methanol (3 times). The number and weight average molecular weights, $M_w = 329000$ and $M_n = 214000$

(polydispersity $M_w/M_n = 1.54$) of the polymer were determined by GPC measurement with polystyrene as the calibration standard. DHF-PPV was soluble in THF, toluene, chloroform and other common organic solvents and formed good uniform transparent thin films on the ITO-coated glass substrates through spin coating the filtered polymer solution from toluene.



Scheme 1. Synthetic route of DHF-PPV.

Figure 1 shows the UV–vis absorption and photoluminescence (PL) spectra of the polymer, DHF-PPV in solution and as solid film, together with EL spectrum of the LED with the structure of PEDOT:PSS/DHF-PPV. DHF-PPV film was prepared by spin coating on a quartz plate. The UV–vis absorption spectra of polymer film and solution agree with each other, while the bandwidth for the solution is narrower than that for the film. This result can be taken as evidence that the conformational differences in the polymer backbone change the effective conjugation lengths and, hence, the spectral characteristics of the polymer.¹² The energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), taken from the onset of the absorption spectrum, was determined to be 2.52 eV ($\lambda_{\text{onset}} = 490$ nm). There is much difference between the photoluminescence spectra of the solution and polymer film. The PL spectrum of the dilute solution of polymer on the photoexcitation at 400 nm showed two peaks at 492 and 521 nm with the minor shoulder at 570 nm, while the PL spectrum of polymer film displayed two maximum wavelengths of 502 and 530 nm, which are red-shifted by 10 nm in comparison with that of the dilute solution. The red shift may be attributed to more efficient energy transfer processes in polymer film.¹²

Cyclic voltammetry (CV) was employed to investigate the redox behavior as well as the HOMO and LUMO energy levels of the polymer. The CV result was obtained using a typical three electrode cell under an argon atmosphere at room temperature with 0.1 M tetrabutylammonium perchlorate (Bu_4NClO_4) in acetonitrile as the electrolyte. The polymer film coated on ITO substrate, Pt wire and Ag/AgCl were used as the working electrode, counter electrode, and reference electrode, respectively. The polymer film exhibited irreversible process in both

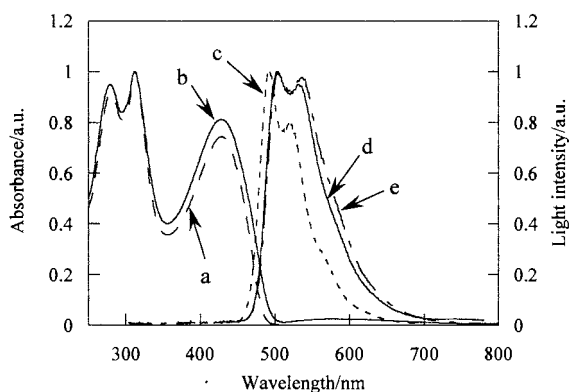


Figure 1. UV-vis absorption (a; CHCl₃ solution, b; film), photoluminescence (c; CHCl₃ solution, d; film), and electroluminescence (e) spectra of DHF-PPV.

oxidation and reduction. The oxidation and reduction onset potentials were measured to be 1.30 and -1.24 V. The electrochemically measured energy gap of the polymer was 2.54 eV, which agrees well with the HOMO-LUMO energy gap of 2.52 eV as measured from the optical absorption measurement. The HOMO and LUMO energy levels of the polymer were calculated from the oxidation and reduction onset potentials to be 5.70 and 3.16 eV, respectively.¹³

Figure 2 shows the current density-voltage (I-V) and luminance-voltage (L-V) relationship for device fabricated using DHF-PPV (130 nm) as the emissive layer, PEDOT:PSS (50 nm) as the hole-injection layer,¹⁴ and Mg-Ag alloy layer (150 nm) as the cathode. By applying the electric voltage, blue-green emission of DHF-PPV was observed at 504 and 535 nm, which very closely resembled the PL spectrum of the polymer film (Figure 1(e)). This means that the same excitations are

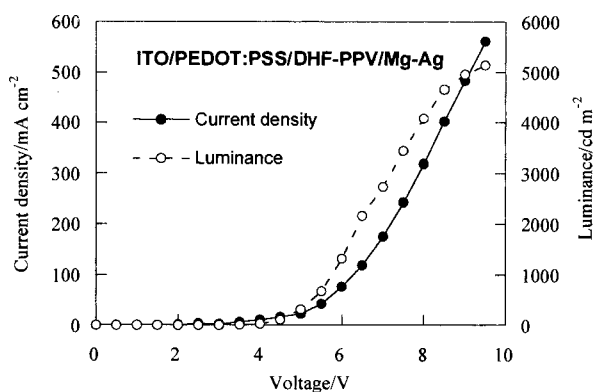


Figure 2. Current density-voltage-luminance characteristics of an ITO/PEDOT:PSS/DHF-PPV/Mg-Ag device.

involved in both cases. Blue-green LED fabricated with DHF-PPV showed turn-on voltage of 3.0 V, and exhibited luminance efficiency and power efficiency of 0.64 cd/A and 0.45 lm/W, respectively, at the luminance of 105.1 cd/m² driven at the voltage of 4.5 V and current density of 16.37 mA/cm². We expect further improvements by reducing the DHF-PPV thickness and using the low work function metal electrode as a cathode.

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- Synthesis of monomer **1** is presented elsewhere in detail. **1**: colorless oil, ¹H-NMR (400 MHz, CDCl₃): δ 7.75–7.70 (m, 2H), 7.51–7.49 (m, 2H), 7.39–7.30 (m, 6H), 4.55 (s, 2H), 4.50 (s, 2H), 2.02 (m, *J* = 5.6 Hz, 4H), 1.13–1.05 (m, 12H), 0.75 (t, *J* = 7.3 Hz, 6H), 0.70 (m, 4H). FAB MS, Found: *m/z* 506. Calcd for C₃₃H₄₀Cl₂: M⁺, 506.25.
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