

## Green Light-emitting diode using a germyl-substituted PPV derivative

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### Abstract

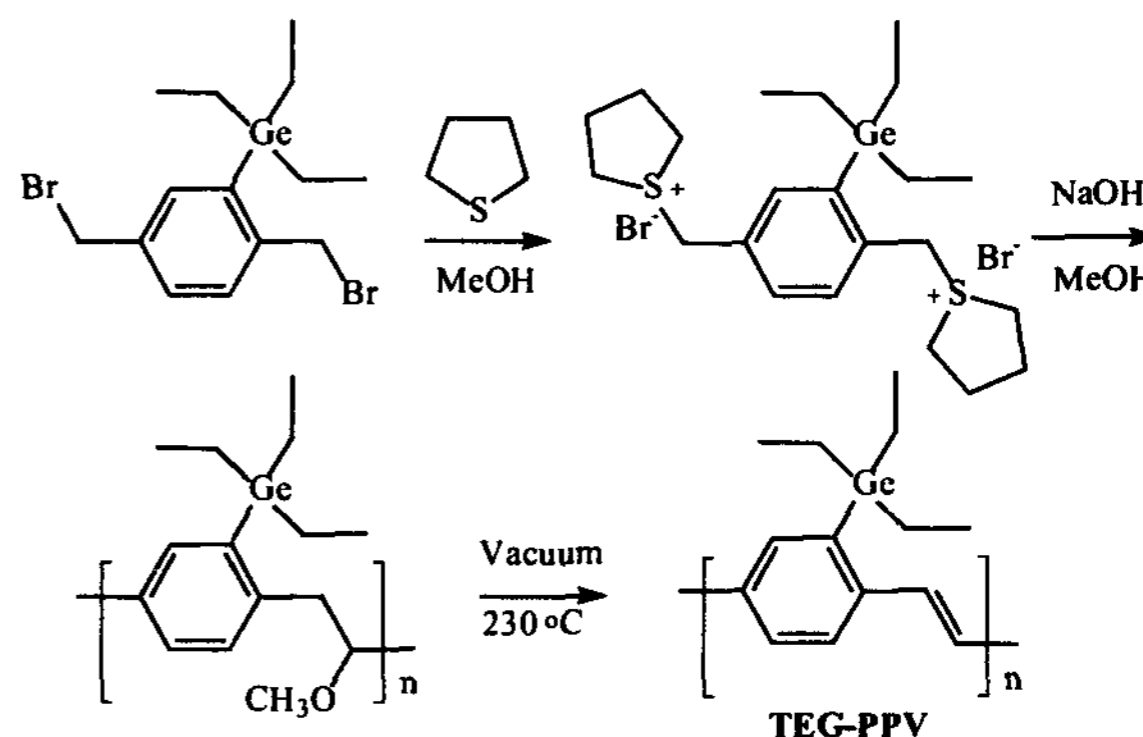
The light-emitting properties of poly(2-triethylgermyl-1,4-phenylenevinylene) (TEG-PPV) are compared with those of the silyl-substituted PPV homologue, poly(2-trimethylsilyl-1,4-phenylenevinylene) (TMS-PPV). The precursor polymer is solution-processable. After carrying out thermal elimination on the precursor polymer film, the resulting fully conjugated polymer film was found to exhibit high thermal stability in air, and absorption that is shifted to the longer wavelength region owing to the extension of the  $\pi$ -conjugated system. TEG-PPV exhibits efficient green light emission; the maximum PL emission of a TEG-PPV thin film was found to be at 515 nm. The HOMO and LUMO energy levels were also determined using photo-emission spectroscopy. The performance of the TEG-PPV EL device was found to be comparable to that of the TMS-PPV device.

### 1. Introduction

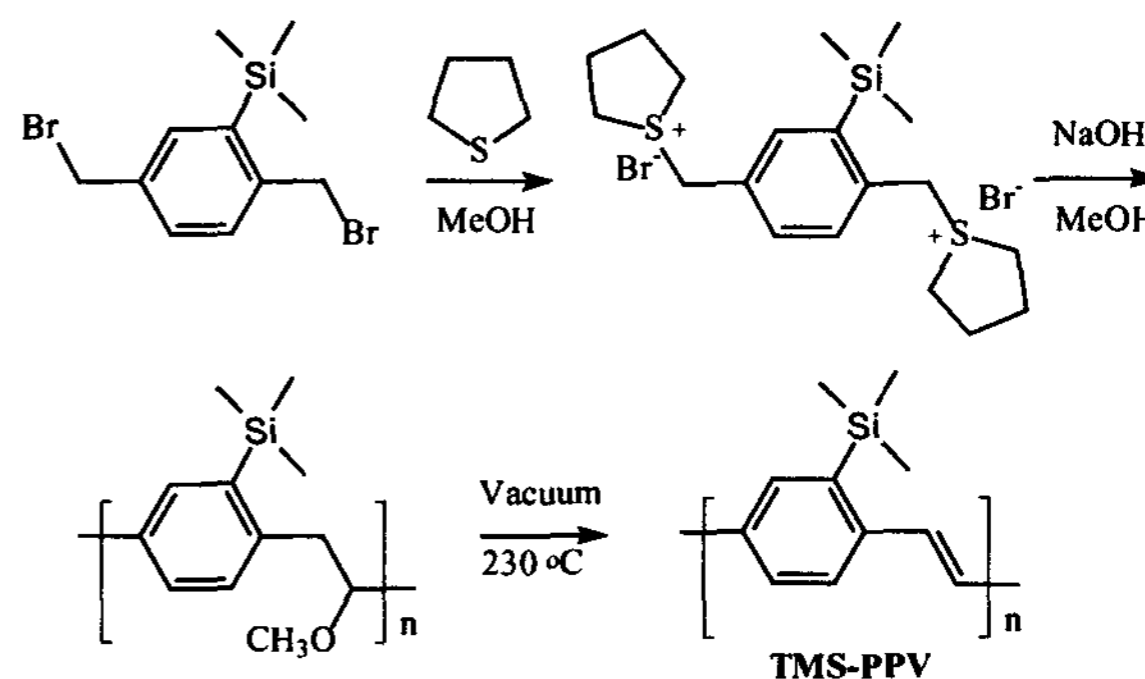
PPV derivatives have attracted much attention as EL materials because of their good mechanical strength, thermal stability, and also color tunability through the introduction of various substituents on the aromatic ring [1,2]. PPV was firstly synthesized via the Wittig polycondensation reaction[3], but this approach yields only an insoluble powder with low molecular weight. In 1968, Wessling and Zimmerman developed a new method for the synthesis of PPV via a water-soluble precursor polymer, as patented by the Dow Chemical Company [4]. More recently, PPV has mainly been synthesized using the dehydrohalogenation reaction route known as the Gilch polymerization because it is regarded as a good synthetic method for obtaining soluble and high molecular weight PPV derivatives suitable for practical applications [5-7].

Here we describe the synthesis of a germyl-substituted PPV derivative via a soluble precursor polymer, and assess its light-emitting properties in comparison with those of the silyl-substituted PPV homologue, poly(2-trimethylsilyl-1,4-phenylenevinylene) (TMS-PPV). The synthetic route and the polymer structure are shown in Schemes 1 and 2.

Scheme 1



Scheme 2



## 2. Experimental

UV-vis and PL spectra were recorded on Jasco V-530 and Spex Fluorolog-3 spectrofluorometers. Thermogravimetric analysis (TGA) was performed on a DuPont 9900 analyzer with a heating rate of 10°C/min under a nitrogen atmosphere. The number average molecular weight and the weight average molecular weight of the polymers were determined using gel permeation chromatography (GPC) on a Waters GPC-150C instrument, with tetrahydrofuran (THF) as the eluent and polystyrene as the standard. The ionization potentials of TEG-PPV and TMS-PPV were measured with a RIKEN Keiki AC-2.[8] The single layer LED devices were fabricated on glass substrates coated with indium-tin oxide (ITO). The device configuration was ITO/TEG-PPV/LiF/Al. EL spectra of the devices were measured using a Minolta CS-1000. Current-Voltage-Luminance (I-V-L) characteristics were recorded simultaneously with the measurement of the EL intensity by attaching the photospectrometer to a Keithley 238 and using a Minolta LS-100 as the luminance detector. All measurements were carried out at room temperature under ambient atmosphere.

## 3. Results and discussion

Figure 1 shows the UV-visible absorption and PL emission spectra of thin films of the organic-soluble precursor polymer and TEG-PPV.

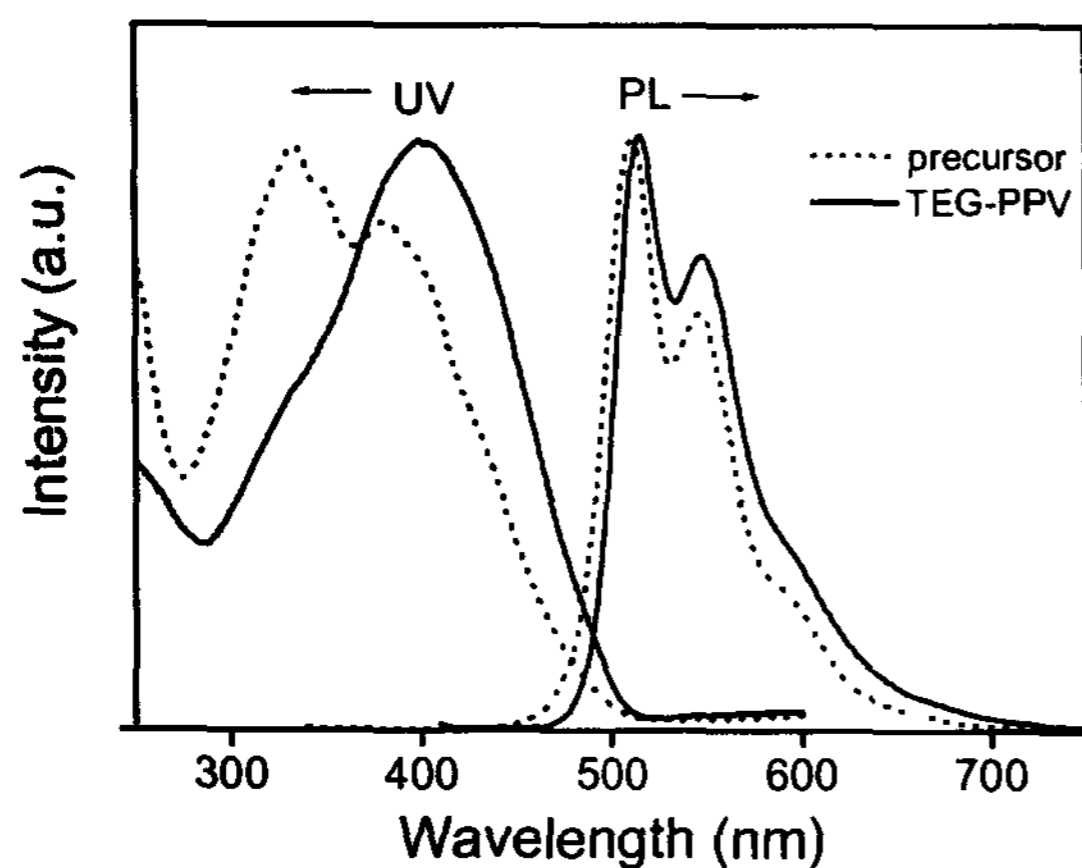


Figure 1. UV-visible absorption and PL emission spectra of the precursor polymer (dotted line) and TEG-PPV (solid line).

The maximum absorption and the absorption edge of the spectra for the precursor polymer arise at 331 and 500 nm respectively. The absorption spectrum of the precursor polymer film has a shoulder peak at about 381 nm because of the  $\pi$ - $\pi^*$  transitions of conjugated segments in the precursor polymer chains. After the precursor polymer film has undergone thermal elimination, its absorption is markedly shifted to the longer wavelength region owing to the extension of the  $\pi$ -conjugated system. The maximum absorption of TEG-PPV is at 399 nm and the absorption edge is at 516 nm, which corresponds to an optical band gap of 2.40 eV. The ionization potential of TEG-PPV was measured using photoemission spectroscopy to determine the energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The measured ionization potential of TEG-PPV using photoemission spectroscopy was 5.70 eV. We estimate the HOMO and LUMO levels to be 5.70 and 3.30 eV respectively, according to the optical band gap determined from the UV-visible absorption edge. The PL spectrum of TEG-PPV has three phonon side bands at 511, 546, and 581 nm. It is interesting to note that the precursor polymer film exhibits a PL spectrum that is almost identical to that of TEG-PPV. The UV-absorption and PL emission spectra of TMS-PPV are almost identical to those of TEG-PPV.

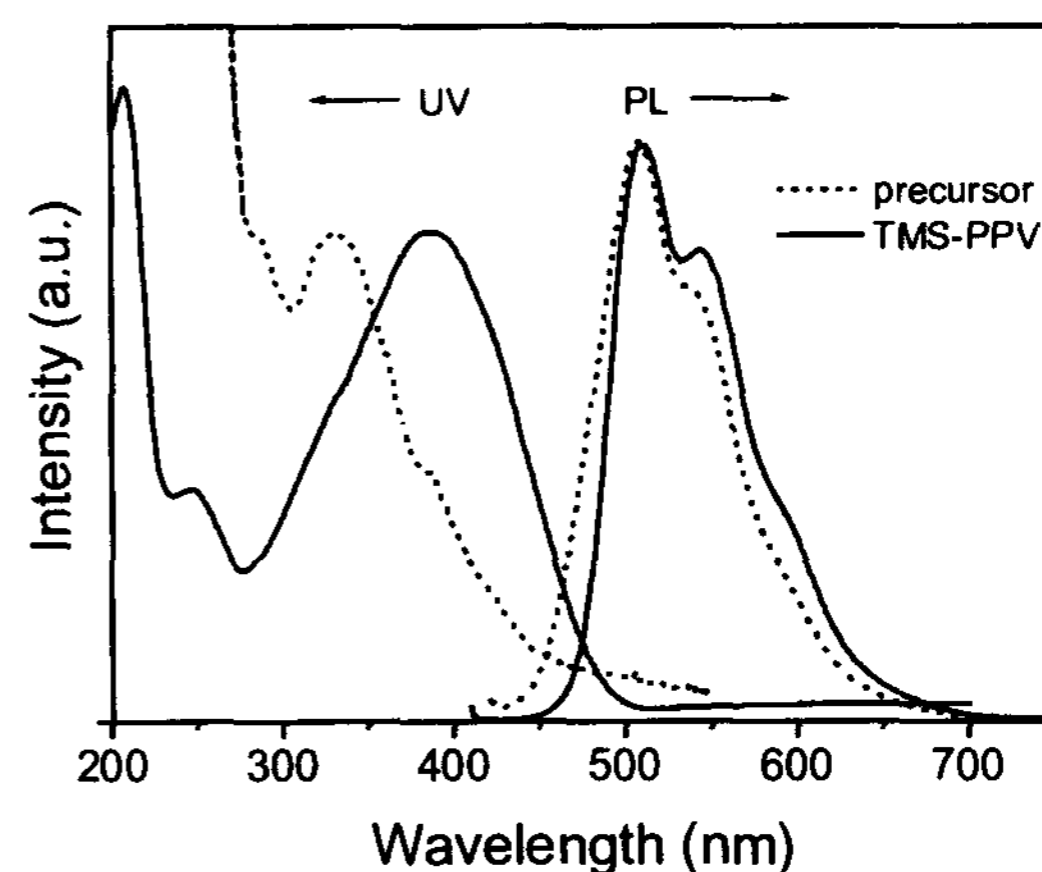


Figure 2. UV-visible absorption and PL emission spectra of the precursor polymer (dotted line) and TMS-PPV (solid line).

Figure 2 shows the UV-visible absorption and PL emission spectra of thin films of the organic-soluble precursor polymer and TMS-PPV. The maximum absorption of TMS-PPV is at 387 nm and the absorption edge is at 500 nm, which corresponds to an optical band gap of 2.47 eV.

Figure 3 shows the EL spectra of the devices, which have ITO/TEG-PPV/LiF/Al and ITO/TMS-PPV/LiF/Al configurations. The EL spectra of both EL devices also exhibit phonon side bands at similar positions to those in the PL spectrum. The performance of the EL device using TEG-PPV is comparable to that of the TMS-PPV device. The EL device using TEG-PPV exhibited a green light emission above 13 V. The maximum brightness and the power efficiency of the EL device using TEG-PPV were found to be 600 cd/m<sup>2</sup> and 1.5 x 10<sup>-2</sup> lm/W respectively, whereas the maximum brightness and power efficiency of the EL device using TMS-PPV were found to be 310 cd/m<sup>2</sup> and 2.5 x 10<sup>-2</sup> lm/W respectively. The characteristics of the EL devices are summarized in Table 2. These preliminary results for the EL device using TEG-PPV are satisfactory, considering that the device was single layered without PEDOT, and also that aluminum, which has a relatively high work function, was employed as the cathode. Thus the germlyl-substituted PPV derivatives are good candidate materials for use in light-emitting diodes.

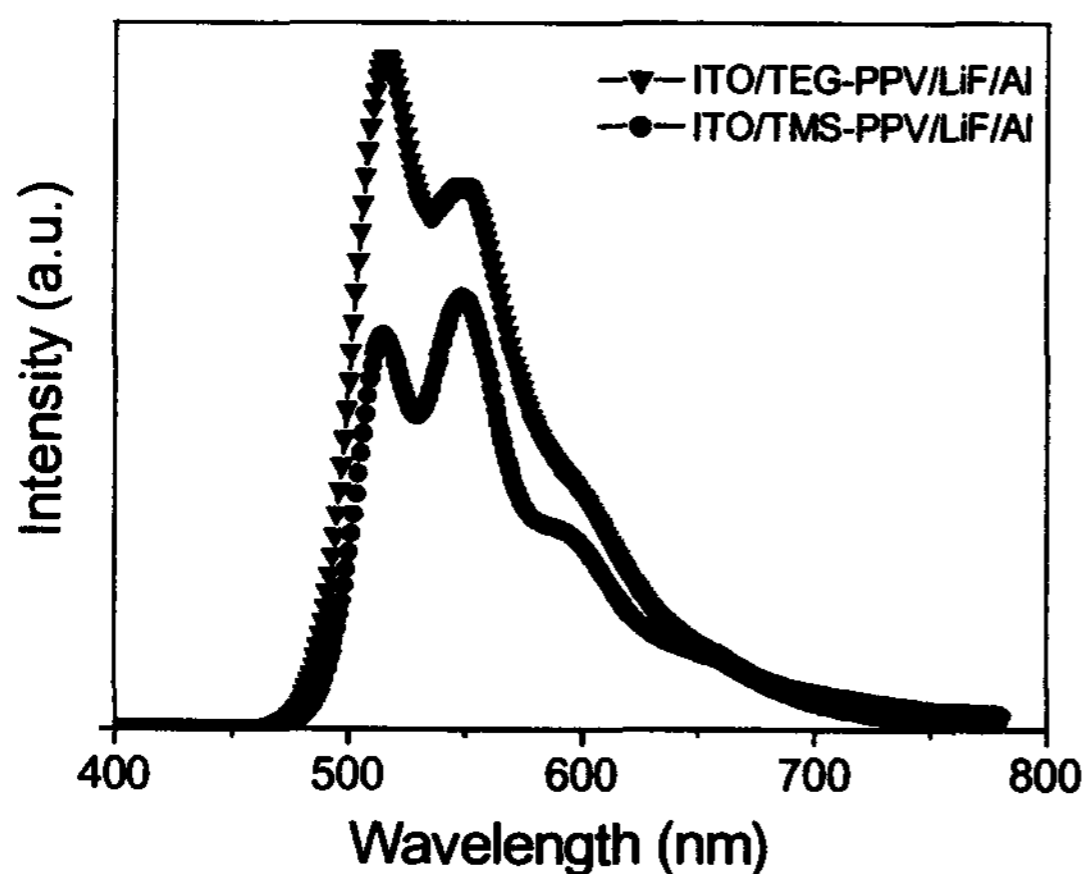


Figure 3. EL spectrum of the device with an ITO/TEG-PPV/LiF/Al configuration.

Further optimization of these EL devices by employing charge-transport layers or lower work function metal electrodes, and also through the introduction of a long alkylgermyl group for Gilch route synthesis, are currently under investigation.

#### 4. Conclusion

We have reported the novel synthesis of a germlyl-substituted PPV derivative via an organic-soluble precursor. The synthesized TEG-PPV exhibits PL emission in the green region of the spectrum. A single layer EL device with an ITO/TEG-PPV/LiF/Al configuration was fabricated and characterized. The EL device using TEG-PPV exhibited comparable performance to a device using a silyl-substituted PPV homologue.

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