

Effect of Substitution of Crown Ether on the Luminescence Performances of PPV

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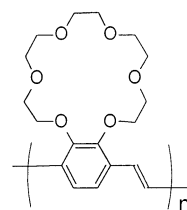
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Photoluminescence (PL) and electroluminescence (EL) properties of a poly(*p*-phenylenevinylene) (PPV) derivative containing crown ether (C-PPV) were investigated. The PL quantum yield as high as 90% in solution and a temperature independence were observed. We infer that the surrounding side group, crown ether, effectively confines the excitons for radiative emission. The planar structure of crown ether also increases interchain interactions in the polymer and induces the formation of aggregation, which makes the PL spectrum of its solid film red-shifted. Through the Langmuir–Blodgett method, the evidence for aggregate formation is demonstrated. The polymer has been used in light emitting diodes. Using C-PPV as an emitting layer, the single layer device shows a low turn-on voltage (ca. 3 V), whereas the double layer device with a structure of ITO/C-PPV/tris(8-hydroxyquinolino)aluminum (Alq₃)/Al shows a moderate EL performance with a brightness of 730 cd/m² and an external efficiency of 0.04%.

1. Introduction

Since the discovery of polymer light-emitting diodes (LEDs) in 1990,¹ a wide variety of conjugated polymers have been developed as electroluminescent (EL) materials.^{2–4} Among these materials, polymers containing the chromophore of phenylene vinylene (PV) are well-studied.^{5,6} However, the relatively low photoluminescence (PL) quantum efficiency (~27%) of poly(*p*-phenylene vinylene) (PPV)⁷ motivates further consideration of molecular engineering that can be used to improve the optical and electric properties as well as other properties, such as the processibility of the polymer. Current research efforts in these conjugated PPV derivatives include attachment of side substituents to improve the processibility, color tuning via random introduction of saturated carbons along the PPV backbone and via synthesis of block copolymer, as well as luminescence enhancement through polymer chain disorder and attachment of bulk phenyl side groups.⁸ Early in 1993, Greenham and his colleagues had synthesized a soluble highly fluorescent poly-(cyanoterephthalylidene)s (CN-PPV) in which each arylene fragment carries solubilizing long-chain alkoxy substituents.⁹ Substitution of the electron withdrawing cyano group on the polymer backbone lowered the HOMO and LUMO energy states and enhanced the EL efficiency. Some other PPV derivatives such as poly(2-methoxy-5-(2'-ethylhexyloxy)-*p*-phenylenevinylene) (MEH-PPV) have also been synthesized. To date, the substituents used to improve the processibility are mainly alkyl, alkoxy, silyl, and phenyl groups. In this paper, we report a synthesized PPV derivative: crown ether-containing poly(*p*-phenylenevinylene) (C-PPV). The introduction of crown ether substitutes, as realized for the PPV derivative, greatly increased the solubility and improved PL properties. PL quantum yield about 90% in solution is achieved. On the other hand, crown ether exerted little effect on the band gap with respect to PPV, which enabled the emission of yellow-green light. By using this PPV derivative as an emissive material, we also performed



C-PPV

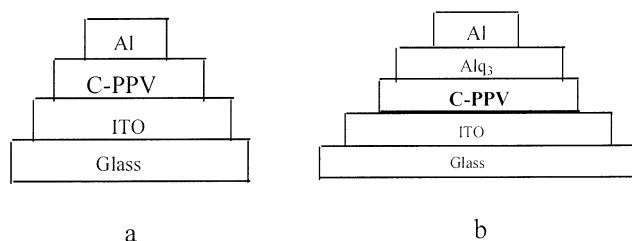


Figure 1. Chemical structure of C-PPV and configurations of the devices.

organic light emitting devices with simple structure. Low threshold and a moderate external EL efficiency were achieved.

2. Experimental Section

C-PPV was synthesized via a modified Gilch route.¹⁰ In contrast to the very low molecular weights of C-PPVs reported by other papers,^{11,12} the weight average molecular weight (M_w) of this molecular reached 8.69×10^4 , determined by a laser light scattering analysis. In Figure 1, the chemical structure of C-PPV and the LED configurations are given. C-PPV was used as an emitter material. The substrate was an indium–tin-oxide (ITO)-coated glass, which was cleaned by ultrasonication in water, alcohol, chloroform, and acetone consecutively for 10 min each and then was dried. LEDs were fabricated using Al as a cathode, ITO as an anode, and tris(8-hydroxyquinoline) aluminum (Alq₃) as the electron-transporting layer. Alq₃ and the Al electrode were deposited by vacuum evaporation at a

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pressure below 10^{-5} Torr, whereas the C-PPV film was prepared by spin-coating from its chloroform solution. The active area of devices was about 7 mm^2 . Cyclic voltammetry (CV) of the thin film of C-PPV was performed on a computer-controlled EG & G potentiostat/galvanostat model 283 with a three-electrode cell. Absorption and photoluminescence spectra were studied for thin films using quartz substrates. The Langmuir-Blodgett (LB) films of C-PPV were fabricated on KSV-5000 (Finland) computer controlled Langmuir alternating troughs. EL spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer with the LED forward biased. UV-vis absorption spectra were recorded with a Hitachi U-3010 UV-vis recording spectrophotometer. The power of EL emission was measured using a Newport 2835-C multifunction optical meter. Photometric units (cd/m^2) were calculated using the forward output power and the EL spectra of the devices, assuming Lambertian distribution of the EL emission. The Commission Internationale de L'Eclairage coordinates were measured using a PR-650 SpectraScan SpectraColorimeter. Current-voltage characteristics were measured with a Hewlett-Packard 4140B semiconductor parameter analyzer. All of the measurements were performed under ambient atmosphere at room temperature.

3. Results and Discussion

The optical absorption spectra of C-PPV in CHCl_3 solution and as thin film are shown in Figure 2. The π - π^* transition peak and the absorption edge of C-PPV (film) appear at 458 and 523 nm, respectively. In the case of PPV, the π - π^* transition peak and the absorption edge are at 415 and 525 nm, respectively.¹³ Compared with PPV, the π - π^* transition peak of C-PPV is red-shifted by 43 nm, whereas the absorption edge is almost the same. The energy band gaps of PPV and C-PPV, which are calculated from the absorption edges, are 2.36 and 2.37 eV, respectively, implying that the substitution of crown ether on benzene rings has little effect on the π -electron delocalization of the polymer main chain. Moreover, the absorption maximum and edge of C-PPV as thin film are red-shifted compared with that in solution (Figure 2, solid line). This might be because an aggregation is formed in the film or the effective conjugation is increased.

The polymer shows strong luminescence in chloroform. Its luminescence quantum yield in chloroform was measured relative to a standard solution of Rhodamine 6G, whose absolute quantum efficiency is about 0.95. The concentrations of these two materials were adjusted to be 10^{-6} mol/L . The quantum yield is calculated from the following equation:¹⁴

$$\Phi_s = \Phi_r \frac{F_s A_r (n_r)^2}{F_r A_s (n_s)^2} \quad (1)$$

In the above expression Φ is the fluorescent quantum yield, F is the integration of the emission intensities, n is the index of refraction of the solution, and A is the absorbance of the solution at the exciting wavelength. The subscripts r and s denote the reference and unknown samples, respectively. Table 1 lists PL efficiencies of PPV derivatives. It clearly shows that the substitution of crown ether greatly improves the PL property and that C-PPV has the highest luminescence quantum yield (0.90) among the PPV derivatives. It has been reported that one approach for attaining high PL efficiency and solubility is to design alternating rigid conjugated segments and flexible nonconjugated segments along the polymer backbone. The interruption of the π conjugation will effectively confine the

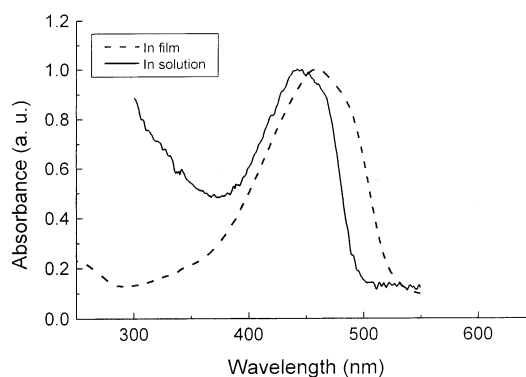


Figure 2. UV-vis absorption spectra of C-PPV.

TABLE 1: PL Efficiencies of PPV Derivatives

polymer	PL efficiency (%)	ref
PPV (film)	0.27	7
MEH-PPV (solution)	0.2–0.35	15
CN-PPV (solution)	0.52	15
C-PPV (solution)	0.90	this work

exciton within the conjugated segments.^{16,17} Attaching methoxy side groups to different positions of the benzene rings has also been used to enhance the exciton confinement.¹⁶ Here, the strong luminescence of C-PPV may be due to the exciton confinement caused by the substitution, crown ether. We measured the temperature dependence of the PL of C-PPV from 273 to 318 K. When the temperature changed, the shape and integrated intensity of the spectrum did not change significantly as compared with that at room temperature, which shows that the thermal deactivation of excitons is limited.

Figure 3 shows the PL spectra of C-PPV as thin film and in solution. The PL spectrum of C-PPV in solution shows an emission peak at 490 nm and a secondary emission at 525 nm on photoexcitation at 450 nm. Compared with that of C-PPV in solution, on photoexcitation at the same wavelength, the emission of C-PPV as thin film is red-shifted and has only one peak at around 534 nm, which is comparable to the secondary emission of the C-PPV solution. Previous studies have provided substantial evidence that the new peak and quenching are the result of interpolymer π -stacking aggregation.^{17–24} To understand the origins of the present PL, photoluminescence excitation spectrum for the polymer was also measured. Difference was found in the normalized PL excitation spectrum from 300 to 500 nm by collecting the emission intensities at various wavelengths (500 and 531 nm), indicating the existence of aggregates. To prove the red shift is a result of the interpolymer π -stacking aggregations, the LB technique was also performed. Substitution of crown ether on benzene rings makes insoluble PPV easily soluble in common organic solvents and suitable for fabricating thin films by the LB technique. Figure 4 shows the surface pressure-area (π -A) isotherm of C-PPV at 23 °C. The steeply inclining part corresponds to the formation of the solid film, and the high surface pressure of the collapse point of the floating layer up to 25 mN/m indicates the good film-forming behavior of C-PPV. From the π -A isotherm, the limiting area per repeat unit is determined to be 0.45 nm^2 (45 \AA^2). This value is useful for estimating the configuration of C-PPV molecules at the air-water interface. The limiting area per repeat unit is about 1.40 nm^2 estimated by the Corey-Pauling-Koltun (CPK) model if the polymer is fully extended and lies flatly on the water surface. Because the limiting area per repeat unit obtained from the π -A curve is smaller than that estimated from CPK model, the polymer either

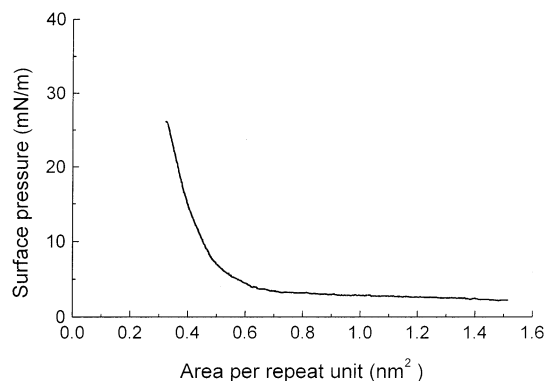


Figure 3. Photoluminescence spectra of C-PPV and electroluminescence spectra of ITO/C-PPV/Al (a) and ITO/C-PPV/Alq₃/Al (b).

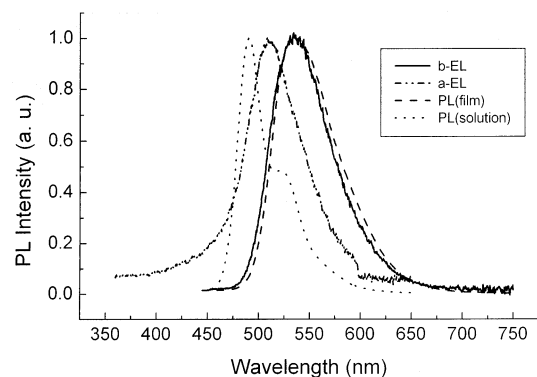


Figure 4. Surface pressure-area isotherm of C-PPV at 23 °C.

takes an entanglement structure or forms π -stacked aggregates by its conjugated π planes face each other and perpendicular/tilt to the air-water interface. The driving force for the entanglement structure probably comes from the π - π interaction. The PL spectrum of the LB films of C-PPV is almost the same as that of its spin-coating film. On the basis of these results, we might conclude that the red shift of PL spectra in both LB films and spin coating film is a result of the interpolymer π -stacking aggregations.

C-PPV with high PL efficiency is expected to be used in LED fabrication. Single layer LED (Figure 1a) was fabricated with C-PPV as the emissive layer. A yellow-green light emission was observed. The emission spectrum is shown in Figure 3 (a-EL), and the Commission International de L'Eclairage coordinates are $x = 0.372$ and $y = 0.576$. The maximum is found to be at 510 nm, which was comparable to that of the PL of the C-PPV (solution), and with the increasing of voltage the spectrum does not change. It indicates that the emission originates from the radiative recombination of singlet excitons within the C-PPV. Figure 5a demonstrates that a low turn-on voltage of electroluminescent emission for the device (about 3.0 V) was achieved. Double layer device with the structure of ITO/C-PPV/Alq₃/Al was also constructed. Figure 5b shows the current-voltage-luminance characteristics of the device, and its EL spectrum is shown in Figure 3 (b-EL). The color was yellow-green with the emission peak at 534 nm (the CIE color coordinates are $x=0.439$, $y=0.536$), which was almost identical to the PL peak position of C-PPV film. A brightness at 7.3 mA and an external efficiency of the two layer device reached 730 cd/m² and 0.04%, respectively.

CV measurements were employed to investigate the energy levels of the material. An oxidative wave ($E_{\text{onset}} = 1.00$ vs Ag/Ag⁺) was observed under an anodic sweep. The energy value of the highest occupied molecular orbital (HOMO) was calcu-

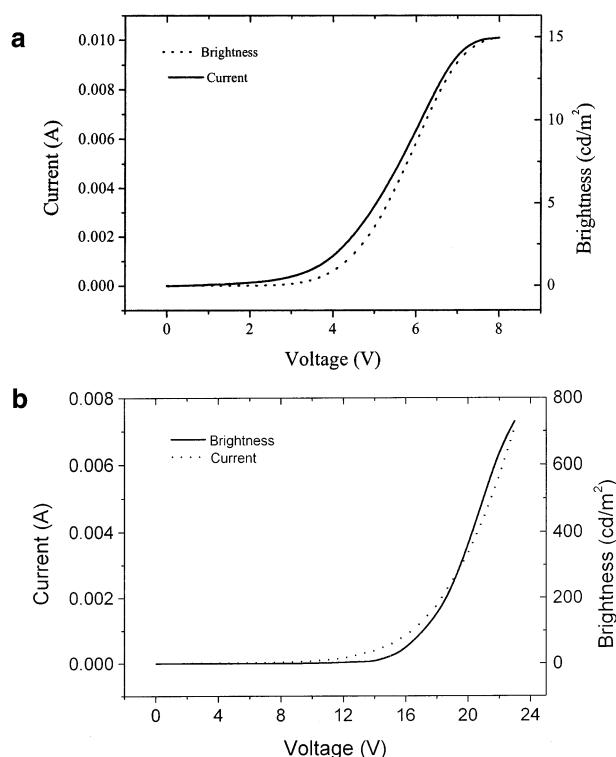


Figure 5. Electroluminescence intensity and current as a function of voltage of ITO/C-PPV/Al (a) and ITO/C-PPV/Alq₃/Al (b).

lated to be -5.68 eV by using ferrocene (Fc) value of -4.80 eV below the vacuum level ($E_{\text{Fc}} = 0.12$ V vs Ag/Ag⁺).²⁵ From the extrapolation of the absorption spectrum, the π - π^* energy band gap of C-PPV was determined to be 2.37 eV ($\lambda_{\text{onset}} = 523$ nm). Hence, the energy value for LUMO of C-PPV should be -3.31 eV. It has been reported that the LUMO and HOMO of PPV are -2.46 and -4.82 , respectively.¹³ The introduction of substituents lowers the HOMO and LUMO energy states.

4. Conclusions

A synthesized PPV derivative, crown ether containing poly(*p*-phenylenevinylene), was reported, and its PL and EL properties were characterized. C-PPV shows high PL quantum yield (about 90%) and an independence of temperature. We deduce that it is attributed to the confinement effects of crown ether. Compared with the emission of C-PPV in solution, that of C-PPV as thin film is red-shifted. Through the PL excitation spectrum and LB technique, we demonstrate that the red shift is a result of the interpolymer π -stacking aggregations. With a structure of ITO/C-PPV/Alq₃/Al, a moderate efficiency device is demonstrated. The introduction of crown ether also lowered the HOMO and LUMO energy states.

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