Dyes and Pigments, Vol. 38, Nos 1–3, pp. 49–56, 1998

PII: S0143-7208(97)00089-2
0143-7208/98 $19.00+0.00

A New Dithiosquarylium Dye for use as an Electron Transport Material in an Organic Electroluminescent Device having Poly(*p*-phenylene vinylene) as an Emitter

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(Received 21 July 1997; accepted 29 August 1997)

ABSTRACT

*A new dithiosquarylium (DTSQ) dye was examined as an electron transport material in organic EL devices. We fabricated the EL cell with poly(*p*-phenylene vinylene)(PPV) as the emission layer. DTSQ was found to be useful as a novel electron transport material. The EL device with DTSQ as the electron transport layer was more efficient than that with only the PPV layer. © 1998 Elsevier Science Ltd. All rights reserved*

Keywords: Electroluminescence (EL), dithiosquarylium dye, electron transport material, poly(*p*-phenylene vinylene) (PPV).

INTRODUCTION

Organic thin film electroluminescence (EL) devices have attracted much attention in accessible flat panel displays; bright and low-voltage driven devices have been reported, in which low-molecular-weight compounds were used as light emitting materials (LEM) and hole transport materials, (HTM) [1, 2].

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The primary advantage of using organic materials as the EML is the availability of highly luminescent organic molecules throughout the entire visible region, making possible the fabrication of a full-color display panel. The attainment of high performances in organic EL devices, i.e. high luminescence, full color emission and improved durability, is still a problem. High performance EL devices are composed of thin organic multilayers, viz. the hole transport layer (HTL), electron transport layer, (ETL) and emission layer (EML). These organic multilayers are sandwiched between a transparent indium-tin-oxide (ITO) cathode and metal anode with a small work function. In order to achieve high performances in organic EL devices, it is necessary to develop not only LEM but also HTMs and ETMs. Fully π-conjugated polymers have been intensively investigated and much effort has been concentrated on the EL devices made of conjugated polymers [3, 4].

It is well established that polymeric materials have good processability and an intrinsically high durability. Because of these advantages, polymeric materials can be anticipated to be of value for EL materials. Among various conjugated polymers, poly(*p*-phenylene vinylene) (PPV) is the most typical example. Polymeric light emitting diodes have gained considerable attention since 1990, when it was reported [3] that PPV devices exhibit electroluminescence [5–8]. Esteglamatian observed a shift of the photoluminescence (PL) peak by doping PPV with a lithium salt [9]. Pei obtained a low threshold voltage and improved durability through electrochemical doping on opposite sides of a thin film of conjugated polymer [10].

In this study, our objective is to design and synthesize a dithiosquarylium (DTSQ) dye which could be used as an ETL layer in organic EL devices having PPV as an emitter.

EXPERIMENTAL

General

Melting points were determined using a Electrothermal IA900 instrument and are uncorrected. Visible and IR spectra were measured using a Shimadzu UV-2100 and a Nicolet Magna IR500 Spectrophotometer, respectively. Elemental analyses were recorded on a Carlo Elba Model 1106 Analyzer. 2,4-Bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide (Lawesson's reagent), hexamethylphosphoramide(HMPA), α,α'-dichloro-*p*-xylene and tetrahydrothiopene were used without further purification. Electroluminescence spectrum was obtained on an Optical Multichannel Analyzer (EG & G, USA) equipped with an OMA4 CCD detector.

Synthesis of PPV precursor and thermal conversion to PPV (Scheme 1)

A mixture of α,α'-Dichloro-*p*-xylene (5 g; 28.56 mmol) and tetrahydrothiopene (13.14 g; 149 mmol) in methanol (80 ml) was stirred for 19 h at 50°C under an N_2 atmosphere. The reaction mixture, after cooling, was poured into cold acetone and the precipitate was filtered and dried under vacuum for 48 h to give 6.64 g of *p*-phenylene dimethylene-1,1-bis(tetrahydrothiopene-1-ium)dichloride (yield = 66.2%).

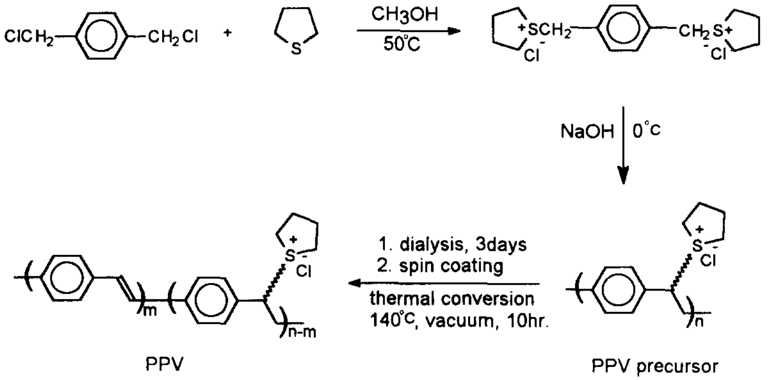
Elemental analysis: C, 54.69; H, 6.88; S, 18.25% (calculated) and C, 54.69; H, 7.26; S, 17.87% (found).

Aqueous NaOH (0.4 mol litre^{-1}; 14 mmol) was added dropwise to the disulfonium salt (5.0 g, 14 mmol) solution in methanol (45 ml) over 20 min, at 0°C. The reaction mixture was stirred for a further 60 min, giving a highly viscous PPV precursor solution. The precursor solution was dialyzed against deionized water at room temperature for 3 days with a cellulose membrane (cut limit *ca* 12000 g mol^{-1}). Dialyzed PPV precursor solution (0.5 wt.%) was spin coated onto ITO glass. The ITO glass coated with the PPV precursor was placed in a vacuum chamber and thermally converted to PPV at 140°C for over 10 h

Synthesis of dithiosquarylium dye (DTSQ) (Scheme 2)

The squarylium dye (SQ) used as starting material was prepared using the previously described procedure [11].

1 g (2.5 mmol) of SQ and 1.2 g (2.5 mmol) of 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-sulfide (Lawesson's reagent) were suspended in a mixture of 15 ml xylene and 1 ml of hexamethylphosphoramide (HMPA).



Scheme 1 Synthesis of PPV precursor and thermal conversion to PPV.

Scheme 2 Synthesis of dithiosquarylium dye, (DTSQ).

The suspension was refluxed for 5 h under efficient stirring. The mixture was evaporated and chromatographed on silica gel (Waco-gel C-300, chloroform) to give 1.93 g of DTSQ. Yield 39%, m.p. 269°C, UV-Vis ($CHCl_3$) λ_{max} ($\varepsilon \times 10^{-5}$): 660 (0.96) nm. Calculated for $C_{28}H_{28}N_2S_2$: C, 73.35; H, 6.13; N, 5.93; S, 13.73; found; C, 73.68; H, 6.13; N, 6.13; S, 14.04.

Fabrication of EL devices

An ITO glass coated glass sheet (ITO layer thickness, 1.08 mm and resistance, 30Ω/□) was cut into 2.5 cm×2.5 cm sections and the electrode area was etched by electrolysis. Cleanliness of the surface of the ITO substrates was crucially important in obtaining a high-performance EL device; this was effected by cleaning in an ultrasonic bath with acetone, methanol and a mixture of isopropyl alcohol and water (1:1 by vol.).

Two kinds of EL devices, ITO/PPV/Mg and ITO/PPV/DTSQ/Mg, were fabricated. The PPV precursor aq. solution was spin coated under 1500 r.p.m. for 15 s and then dried at room temperature for 30 min. The PPV layer was thermally converted at 140°C for 10 h. For fabrication of the ITO/PPV/DTSQ/Mg EL device, a solution of 0.1 wt.% of DTSQ in dichloromethane containing 2 wt.% polyvinyl butyral was spun on the PPV layer.

The Mg metal electrode was deposited by the E-beam method at 20Å s^{-1} rate to 4000Å thickness. The composition for the EL devices is shown in Fig. 1.

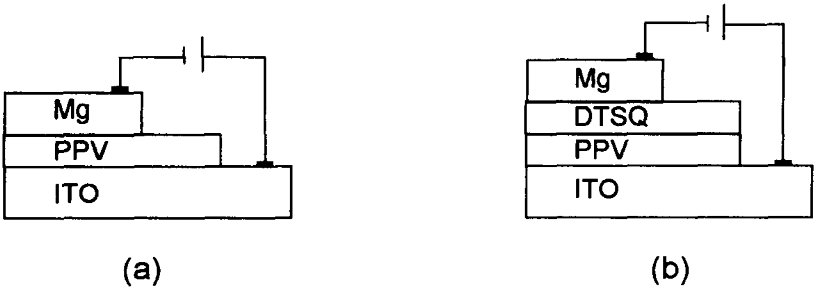


Fig. 1. EL device configuration of (a) ITO/PPV/Mg and (b)ITO/PPV/DTSQ/Mg.

RESULTS AND DISCUSSION

Generation of light in an organic multilayered EL system is the result of recombination of holes and electrons injected from the electrodes. Such recombination in the emitting layer then excites the emitter materials. The properties of the electron transport material are important in the performance of EL devices.

Squarylium dyes have been studied with respect to their ability to color optical recording media [12], in organic solar cells [13] and as electrophotographic photoreceptor [14, 15]. Many ETM which behave as an LEM have been reported. For example, tris(8-quinolinolate)aluminium (Alq_3) is well known to be one of the best ETM, and many other LEMs are also reported. Many different types of organic dyes have been reported to be useful for LEMs, but there appear to be no reported studies on properties of organic dyes as an ETM.

We have now found that a thio-analogue of SQ can be synthesized by the reaction of the SQ dye with Lawesson's reagent. We have previously reported the syntheses characteristics and electrophotographic properties of new dithiosquarylium, (DTSQ) dyes [16]. In order to evaluate the characteristics of DTSQ as ETM, we compared the performance between ITO/PPV/Mg and ITO/PPV/DTSQ/Mg EL devices. The EL spectrum is identical to the PL spectrum of PPV around 540 nm, which indicates that the EL originates from PPV. ITO/PPV/Mg devices utilizing DTSQ on the PPV layer exhibit yellowish green EL, and their EL spectra are identical to the above case.

The threshold voltage for luminescence is about 12 volts in the ITO/PPV/Mg cell. On the other hand, the ITO/PPV/DTSQ/Mg device incorporating the DTSQ layer has a lower threshold voltage of 6 volt. The maximum luminance was achieved at 20 volt for a cell of ITO/PPV/Mg, and at 18 volt in ITO/PPV/DTSQ/Mg. The maximum luminance of the ITO/PPV/DTSQ/Mg device was higher than that of the ITO/PPV/Mg cell. Thus, insertion of the DTSQ layer on the PPV enhances the intensity of luminance.

Figure 2 shows the maximum EL intensity behaviour of the ITO/PPV/Mg and ITO/PPV/DTSQ/Mg device and Fig. 3 shows the current voltage characteristics in the two devices. Current increased as the applied voltage increased, the current being approximately proportional to the bias voltage. Figure 3 shows that ITO/PPV/Mg device needs higher electric power than the ITO/PPV/DTSQ/Mg device. The EL properties of the ITO/PPV/DTSQ/Mg device showed the high performance EL at lower current, as compared with that of the ITO/PPV/Mg device.

It can be concluded that DTSQ acts as an ETL in the EL cell containing PPV and gives a high EL intensity and lowering current density. DTSQ as an ETL plays an important role in transporting electrons and blocking holes,

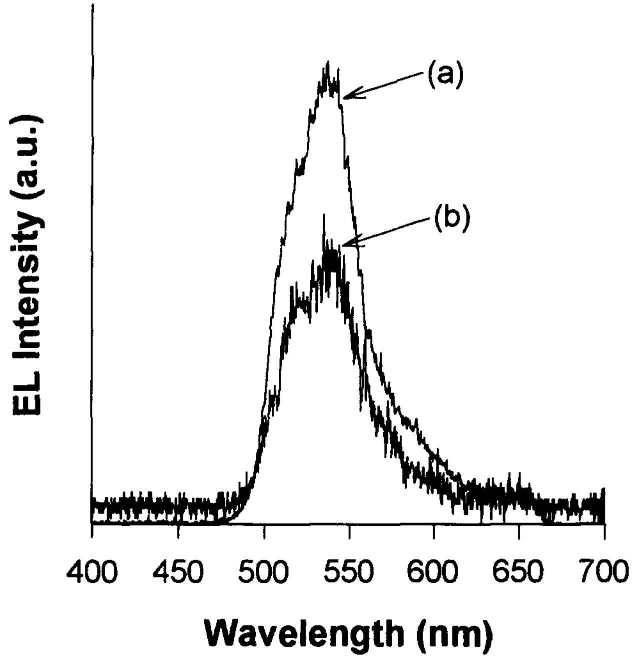


Fig. 2. Maximum EL spectrum of (a) ITO/PPV/DTSQ/Mg cell at 18 volts and (b) ITO/PPV/Mg cell at 20 volts.

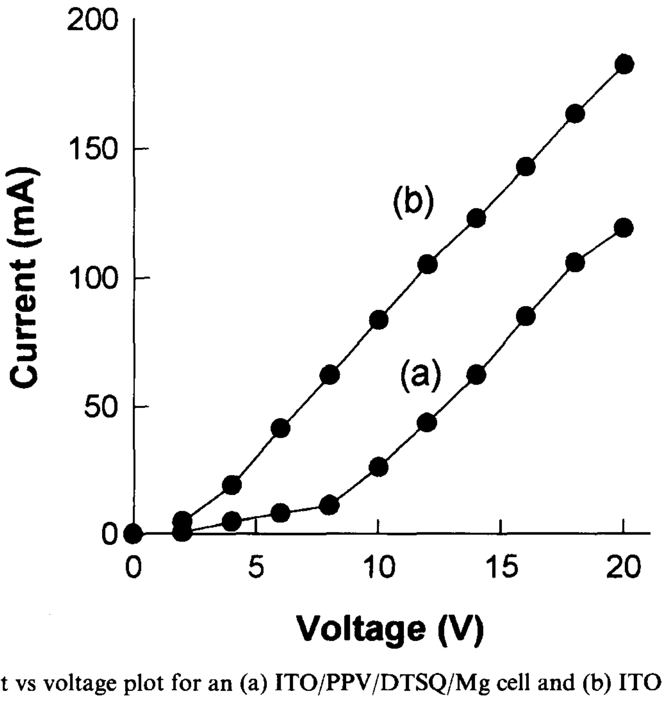


Fig. 3. Current vs voltage plot for an (a) ITO/PPV/DTSQ/Mg cell and (b) ITO/PPV/Mg cell.

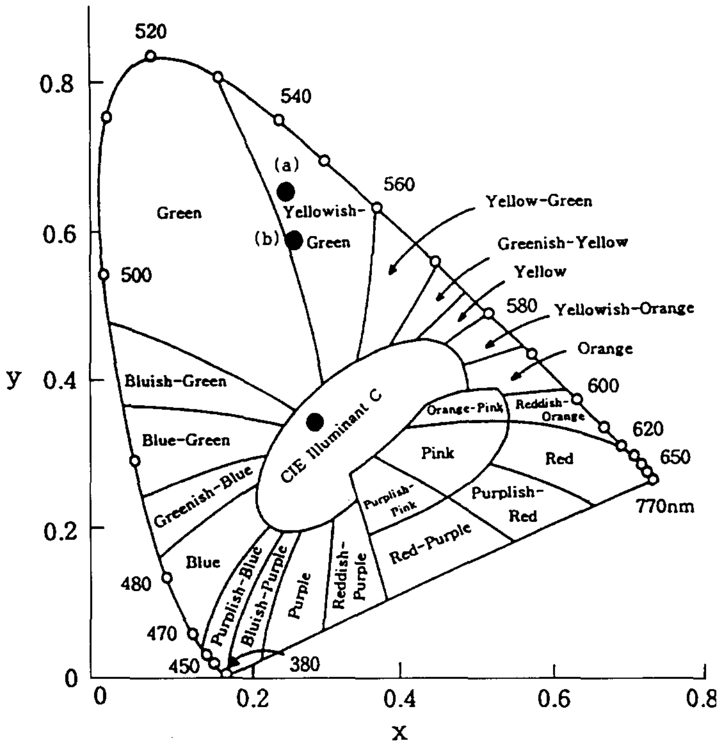


Fig. 4. CIE chromaticity diagram. Color co-ordinates (a) ITO/PPV/Mg and (b) ITO/PPV/DTSQ/Mg EL device.

thus preventing holes from moving into the electrode without recombining with electrons.

Figure 4 shows the CIE color co-ordinates of two kinds of EL cell; the wavelength of maximum luminescence is at 540 nm i.e. green to yellowish green.

ACKNOWLEDGEMENT

This study was supported by the Korean Ministry of Education Research Fund Materials in 1996.

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