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Emitting polymers containing cyano groups. Synthesis and photophysical properties of a fully conjugated polymer obtained by Wittig reaction

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Abstract

A new electroluminescent fully conjugated, substituted PPV-related structure was synthesized. The ring-substituted units (2,5 hexadecyloxy and 2,5 cyano) were interspersed by one non-substituted PPV unit. The EL emission was centered at 612 nm (orange). Double layer devices using PPV as a hole-transporting material showed 3000 cd/m^2 at a 20 V bias.

In addition to the better transport characteristics imparted by the PPV layer, Forster transfer at the interface provided a better light output in these devices in comparison with single layer LEDs. Increases in PPV thickness yielded a slight blue shift suggesting that emission from the bulk PPV was occurring as well. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Fully conjugated polymers based on cyano-modified PPV structures feature both good electron transport properties and efficient emissions at longer wavelengths in the visible spectra. The cyano group is responsible for the high electron affinity associated with these structures [1,2], which is a desirable property because more stable metal electrodes, such as aluminum, can be used for electron injection. Further improvement of the device emission efficiency can be obtained by appropriate combination with a hole-transporting material by means of blending or in multilayer configurations. The multicomponent emitter layers allow a balanced injection of opposite charges under forward bias. Also, there is an increase of charge recombination within the emitter layer due to charge confinement by energy barriers built up at the interfaces between the respective components. These effects can increase the EL device efficiency by one or two orders of magnitude.

To improve the solubility and facilitate the processing of thin films on to electrode surfaces of PPV related polymers, bulky side groups are generally attached to the poly(1,4-phenylene vinylene) main chain, such as extended alkoxy or alkyl groups in the 2,5-positions on the aromatic ring. Therefore, the cyano and extended akyl or alkoxy side groups may occupy different relative positions in the PPV chain. The presence and relative position of these groups exert a large influence on the photoluminescent (PL) and electroluminescent (EL) properties [3,4]. The qualitative assessment of these effects on the emission properties of conjugated polymers allows the prediction of a desired color emission by means of systematic modifications of a basic structure.

The substitution effects can be discussed in terms of steric and electronic contributions. The presence of long and bulky alkoxy or alkyl groups in the 2,5 aromatic positions in PPV brings about a weak steric interaction between neighboring units, which in some instances is responsible for a small blue-shift effect [5]. The steric hindrance associated with these side groups in adjacent units prevents their coplanarity, decreasing somewhat the conjugation length and increasing the band gap of the emitting centers [6]. An example is the difference of 75 nm between the emission maxima of 2,5-dicholesteryl-PPV (max. at 530 nm) [7], and 2-methoxy-5-(2-ethylhexyloxy)-PPV (MEH-PPV) (max. at 605 nm) [8]. On the other hand the electron donating property of the alkoxy groups causes a moderate to strong red shift and the net result of these opposing effects is a bathochromic emission compared to PPV itself. These side groups also improve other photophysical properties since they hinder the close packing of the conjugated chains, minimizing non-radiative decays via migration of excitons

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to quenching sites and self-quenching processes [9] thereby increasing the EL efficiency [10]. Further, the interchain excitation caused by the symmetrical substitution of linear side groups has been shown to enhance the PL emission lifetime [11]. Finally the presence of side groups allows the synthesis and purification procedures to be carried out in solution.

Most of the cyano-based PPV structures reported to date have had the cyano function linked to the vinylene group, and this also causes both steric and electronic effects. PPV-like structures bearing only the cyano group as a ring substituent have not been widely synthesized and characterized so far [12–14]. Steric hindrance between cyano groups at the α-vinyl position relative to the alkoxy or alkyl groups present in the 2,5 aromatic positions causes a blue-shift [5]. When the steric hindrance is minimal, cyano-based structures bearing alkoxy groups exhibit a strong red-shift effect when compared to structures bearing only alkyl groups [1,15]. Therefore, dipolar interaction between electron donor/acceptor groups is one of the structural requirements for production of strongly red-shifted emissions [16,17].

Cyano modified PPV structures in which the cyano group is linked to the vinylene group have been synthesized mostly via Knoevenagel reaction between aromatic dialdehydes and dicyanomethyl compounds in the basic media [5,15,18–21]. This method has some drawbacks because side reactions may take place, which precludes the production of defect-free structures. Conjugated polymers bearing cyano groups attached directly to the aromatic ring, which minimizes steric hindrance, have been synthesized via the Wessling soluble precursor scheme [12,14,22] and thermal polymerization of 2,5-diiodo-3,4-dicyanothiophene [23].

In a previous publication [17], we compared the photophysical behavior of two isomeric polymer structures composed of cyano-modified distyryl chromophores. A new structure with the cyano group linked to the central aromatic ring of the chromophore was synthesized by a Wittig reaction. For comparison, another structure with the cyano group linked to the vinylene function was synthesized by appropriate adaptation of a conventional Knoevenagel reaction. The Wittig-type polymerization produced a material with fewer structural defects together with a more strongly red-shifted emission. A monolayer LED device using the Wittig reaction product showed relatively higher emission intensity and stability than the Knoevenagel reaction product. This new technique for preparing cyano-based conjugated polymers via Wittig reaction is extended in this study to produce a full conjugated cyano substituted polymer bearing long alkoxy groups which proved to be an efficient long wavelength emitter.

2. Experimental section

Tetrahydrofuran and toluene were refluxed over 4,4′-methylenebis(phenyl isocyanate) (MDI) and distilled prior to use. Terephthalaldehyde *mono*-(diethyl acetal) (Aldrich) was distilled under reduce pressure and stored under nitrogen. 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), hydroquinone, 1-bromohexadecane, hydrogen bromide (30 wt.% in acetic acid), paraformaldehyde, triethyl phosphite, potassium *tert*-butoxide, Amberlyte IRA904 and Amberlyte 15 ion exchange resins were used without further purification. All others reagents and solvents were used as-received.

2.1. Instrumental characterization

FTIR spectra were recorded on an IBM IR3x type 913X spectrometer equipped with Nicolet PC/IR operation software. Cast films obtained from the evaporation of polymer solutions in chloroform over a KBr cell were used for this purpose; spectra of the low molecular weight compounds were obtained from KBr pellets. ^{1}H and ^{13}C NMR spectra of $CDCl_3$ solutions were taken on a Varian DPX300 spectrometer. GPC and HPLC measurements were taken in a system composed of a Waters 500 Pump, injector U6K, a Waters Lambda-Max481 UV detector. For GPC measurements a series of three Ultrastyragel columns with pore sizes of 10^4, 10^3 and 10^2 Å and calibrated against polystyrene standards were used. THF solutions of the polymer samples were filtered through a Millipore membrane with a porosity of 0.45 μm just before injection. Purity of the low molecular weight precursors was determined by HPLC measurements; two different systems were used depending upon the samples being analyzed. The acronyms for the columns types used from here are: Si-CN, Spherisorb Cyano bonded silica and Si-C_{18}, Spherisorb ODS-2 bonded silica, both with 4.6×250 mm^2 dimensions and stationary phase with 5 μm particle size. Elemental analyses were performed by the University of Massachusetts at Amherst Microanalytical Laboratory. Melting point of the low molecular weight compounds and the polymer thermal transitions were determined using a Perkin–Elmer DSC-7 series differential scanning calorimeter; scans were carried out at rates of 20°C/min. Solid state absorption spectra were taken using a UV/Vis Perkin–Elmer Lambda 9 UV/VIS/NIR spectrometer. Solid state PL spectra were taken using a Perkin–Elmer LS50B Luminescence Spectrometer. Thin films used for spectroscopic measurements were obtained by casting polymer solutions at a concentration of 10^{-4} M onto quartz windows.

2.2. EL device fabrication and measurements

A single layer device was built as follows. Chloroform solutions of the cyano polymer (CP), at a concentration of 5 mg/ml, were filtered through 0.2 μm Millipore. The solution obtained was spin cast onto commercial ITO electrodes. After evaporation, a thin calcium layer was vacuum deposited over the substrate at a pressure below 10^{-7} Torr, and aluminum was subsequently deposited in the same way to prevent the anode from oxidation and improve mechanical resistance of the cathode. All the device preparation and measurement steps were performed under dry argon in a dry box VAC HE-493.

Double layer devices were built by means of spin coating the ITO surface with an aqueous solution of PPV precursor. The thin precursor layer obtained after drying was thermolysed to a PPV layer at 220°C for 3 h under high vacuum. PPV layers with thicknesses of 15 and 90 nm were used. The subsequent steps for the deposition of CP layers were achieved in the same way.

2.3. Synthesis of monomers

*2.3.1. 2,5-dicyano-1,4-xylylene-bis(triphenylphosphonium bromide) (**1**)*

This monomer was synthesized previously here according to the procedures described elsewhere [17]. This monomer showed + 99% purity by HPLC analysis using Si-C_{18} column and a solution of 0.1 wt/vol% of sodium dodecylsulfate, 0.001 M of trifluoroacetic acid in acetonitrile/water 80:20 as solvent.

*2.3.2. 1,4-bis(hexadecyloxy)benzene (**2**)*

This compound was synthesized via a conventional Williamson reaction between hydroquinone and 1-bromohexadecane in the presence of potassium carbonate. The product was crystallized twice from toluene and dried under vacuum

Yield	89.5%
HPLC	97.9% (Si–CN, isooctane, 524 nm detection)
MP	84.0°C
^{1}H NMR ($CDCl_3$) (ppm)	$\delta = 6.82$ (s, 4H), 3.87 (t, 4H), 1.73 (m, 4H), 1.55 (m, 4H), 1.20 (m, 48H), 0.86 (t, 6H)
$C_{38}H_{70}O_2$ (558.97) (%)	Calc.: C = 81.65; H = 12.62
	Found: C = 81.8; H = 12.4
IR (KBr pellet) (cm^{-1})	3036, 2955, 2918, 2872, 2849, 1516, 1473, 1464, 1396, 1383, 1375, 1356, 1292, 1277, 1244, 1192, 1161, 1130, 1109, 1051, 1039, 1030, 1003, 825, 771, 729, 719, 540, 528, 518

*2.3.3. 1,4-bis(bromomethyl)-2,5-bis(hexadecyloxy)benzene (**3**)*

This compound was synthesized from **2** by adapting a procedure for bromomethylation described elsewhere [24]. The product was crystallized from isopropanol and from hexane thereafter.

Yield	52.3%
HPLC	95.5% (Si–CN, cyclohehane, 220 nm detection)
MP	101.3°C
^{1}H NMR ($CDCl_3$) (ppm)	$\delta = 6.97$ (s, 2H), 4.52 (s, 4H), 3.98 (t, 4H), 1.80 (m, 4H), 1.56 (m, 4H), 1.25 (m, 48H), 0.88 (t, 6H)
^{13}C NMR ($CDCl_3$) (ppm)	$\delta = 151.04$, 127.88, 115.01, 69.38, 32.32, 30.09, 29.99, 29.76, 29.16, 26.47, 23.09, 14.52
$C_{40}H_{72}Br_2O_2$ (744.81) (%)	Calc.: C = 64.50;H = 9.74; Br = 21.46
	Found: C = 64.7; H = 9.8; Br = 21.6
IR (KBr pellet) (cm^{-1})	2938, 2916, 2851,1510, 1474, 1456, 1444, 1414, 1394, 1316 1226, 1211, 1047, 1003, 906, 870, 860, 717, 690, 547.

*2.3.4. 2,5-bis(hexadecyloxy)-1,4-xylylene-bis(diethyl phosphonate) (**4**)*

A mixture of 7.4 g (10 mmol) of **3** and 8.6 ml (50 mmol) of triethyl phosphite in 100 ml of dry toluene was refluxed for 20 h. The solvent was vacuum evaporated and the remaining oil was diluted with ethanol. Upon freezing the solution at −40°C, a fine white powder precipitated, and was collected by vacuum filtration. Two other crystallizations from ethanol were carried out in the same way. The product was dried and kept under high vacuum.

Yield	7.5 g (95%)
HPLC	99.5% (Si–CN, cyclohehane/dioxane 90:10, 254 nm detection)
MP	69.7°C
^{1}H NMR ($CDCl_3$) (ppm)	$\delta = 6.91$ (s, 2H), 4.02 (m, 8H), 3.91 (t, 4H), 3.20 (d, 4H), 1.76 (m, 4H), 1.57 (m, 4H), 1.26 (m, 48H), 0.88 (t, 6H)
^{13}C NMR ($CDCl_3$) (ppm)	$\delta = 150.70$, 119.76, 115.25, 69.35, 62.26, 32.30, 30.08, 30.00, 29.84, 29.74, 27.55, 26.52, 25.68, 23.07, 16.73, 14.50
$C_{48}H_{92}P_2O_8$ (797.20) (%)	Calc.: C = 67.10; H = 10.79; P = 7.21
	Found: C = 66.9; H = 10.8; P = 6.9
IR (KBr pellet) (cm^{-1})	3074, 2925, 2853, 1510, 1468, 1458, 1419, 1390, 1367, 1309, 1253, 1213, 1165, 1097, 1057, 1032, 960, 895, 871, 835, 825, 781, 721, 667, 642, 530

*2.3.5. 1,4-bis(4-formylstyryl)-2,5-bis(hexadecyloxy)benzene (**5**)*

A solution of 3 ml (15 mmol) of terephthalaldehyde *mono*-(diethyl acetal) in 30 ml of THF was added dropwise over another solution of 5 g (6.3 mmol) of **4** and 1.45 g (13 mmol) of potassium *t*-butoxide in 60 ml of tetrahydrofuran under nitrogen with stirring. The solution turned from colorless to fluorescent orange after addition, and was stirred at room temperature for 30 min; it was then refluxed for 10 h. 40 ml of 6 N HCl was added and the mixture was refluxed for another 10 min, then added dropwise into 300 ml of cold water. The orange solid obtained was vacuum filtered and crystallized three times from isopropanol.

Yield	2.8 g (48%)
HPLC	99.2% (Si–CN, cyclohehane/ dioxane 95:05, 254 nm detection)
MP	Heating scan: 87.3, 102.3 and 114.3°C Cooling scan: 72.0°C
^{1}H NMR ($CDCl_3$) (ppm)	$\delta = 10.03$ (s, 2H), 7.86 (d, 4H), 7.62 (m, 6H), 7.20 (m, 4H), 4.05 (t, 4H), 1.89 (m, 4H), 1.55 (m, 4H), 1.25 (m, 48H), 0.87 (t, 6H)
^{13}C NMR ($CDCl_3$) (ppm)	$\delta = 191.96$, 151.78, 144.37, 135.58, 130.63, 128.26, 127.28, 111.12, 69.86, 32.32, 30.10, 29.84, 29.76, 26.68, 23.09, 14.52
$C_{56}H_{82}O_4$ (819.26) (%)	Calc.: C = 82.10; H = 10.09; Found: C = 82.0; H = 10.2
IR (KBr pellet) (cm^{-1})	3167, 3121, 3057, 2918, 2851, 2729, 1697, 1624, 1597, 1566, 1512, 1496, 1469, 1427, 1390, 1342, 1319, 1305, 1257, 1209, 1165, 1051, 999, 960, 846, 808, 719, 642, 509

2.4. Synthesis of the polymer

*2.4.1. Poly[1,4-phenylene-1,2-ethenediyl-2,5-bis(hexadecyloxy)-1,4-phenylene-1,2-ethenediyl-1,4-phenylene-1,2-ethenediyl-2,5-dicyano-1,4-phenylene-1,2-ethenediyl] (**6**)*

A solution of 0.75 ml of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in 5 ml of anhydrous THF was stepwise added to a solution of 0.819 g (1.0 mmol) of **1** and 0.838 g (1.0 mmol) of **5** in 5 ml of THF under stirring and nitrogen. After complete addition of the base, the reaction was left to proceed overnight. The reaction was quenched by dropping the mixture into a large amount of methanol acidified with some drops of hydrochloric acid. After three steps of purification by precipitation, the polymer was dissolved in chlorobenzene and was isomerized to the all-*trans* configuration by refluxing with a catalytic amount of iodine for 4 h in the absence of light and under nitrogen. A chromatographic column filled with equal amounts of Amberlyte IRA904 and Amberlyte 15 was thoroughly washed with water, methanol and then with anhydrous tetrahydrofuran. A polymer solution was eluted though this column by a mixture of chloroform/tetrahydrofuran (80:20). The polymer was precipitated by the addition of a large amount of methanol to the eluted solution. Two further precipitations were carried out, and the polymer obtained was filtered and dried under high vacuum.

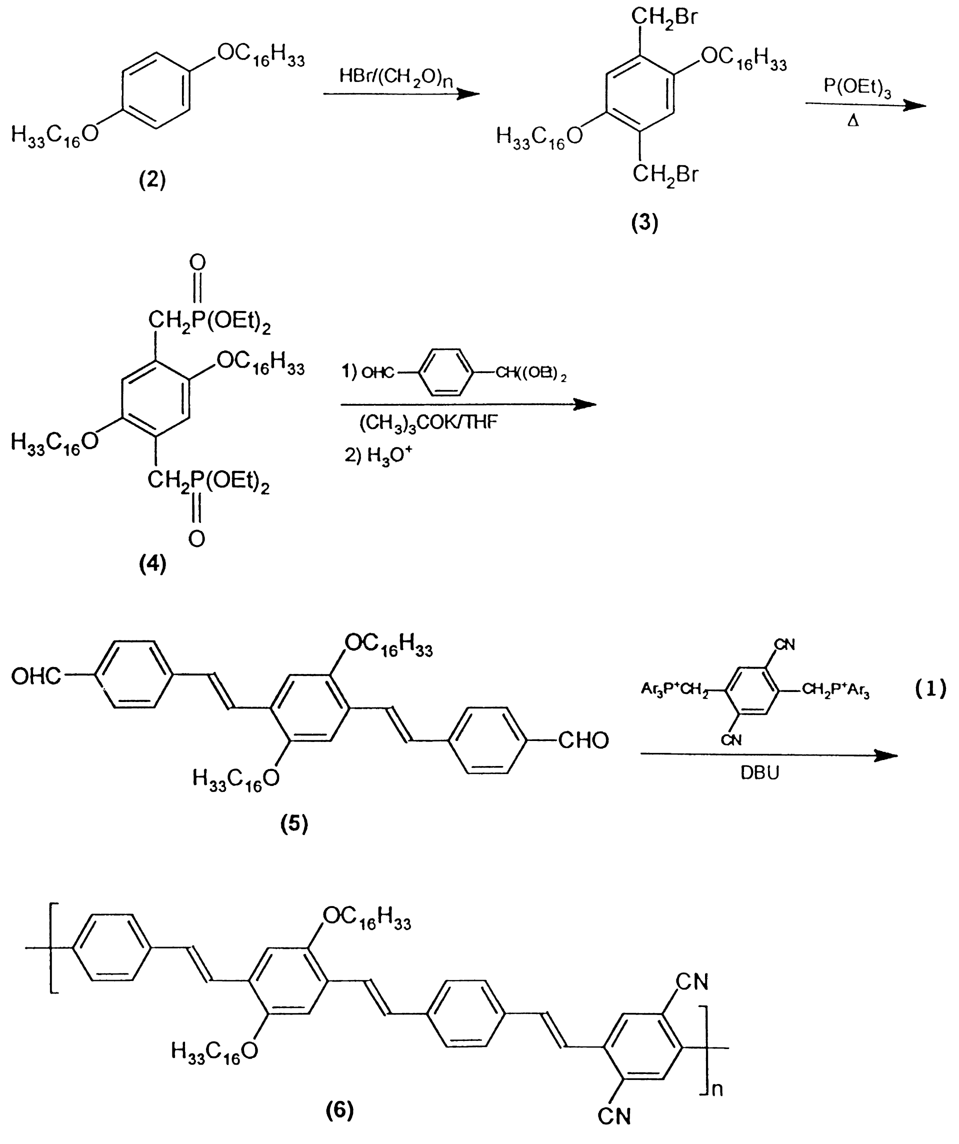
Yield	0.51 g (54.3%)
^{1}H NMR ($CDCl_3$) (ppm)	$\delta = 7.92$, 7.77, 7.57, 7.44, 7.24, 7.01, 1.80, 1.48, 1.17, 0.79
^{13}C NMR ($CDCl_3$) (ppm)	$\delta = 151.52$, 139.23, 134.73, 130.64, 129.44, 128.10, 127.85, 127.38, 127.24, 117.78, 116.99, 69.83, 53.02, 32.32, 30.12, 29.86, 29.77, 26.70, 23.09, 20.39, 14.53
$C_{66}H_{86}N_2O_2$ $(939.42)_n$ (%)	Calc.: C = 84.38; H = 9.23; N = 2.98 Found: C = 83.9; H = 9.5; N = 2.8
IR (KBr, cast film) (cm^{-1})	3040, 2924, 2853, 2226, 1697, 1631, 1595, 1564, 1512, 1493, 1468,1424, 1391, 1345, 1304, 1260, 1210, 1165, 1103, 1036, 965, 860, 856, 808, 721, 515.

3. Results and discussion

3.1. Monomer and polymer syntheses

Scheme 1 shows the synthetic route used to produce the PPV-based polymer bearing extended alkoxy and cyano groups linked to the chromophoric repeating unit. The alkoxy groups provide polymer solubility in organic solvents, and also increase the crystallinity of low molecular weight precursors, improving the purification steps. Monomers of high purity were obtained by successive crystallizations, as verified by chromatographic and elemental analysis.

The polymerization was carried out by reacting a dialdehyde with a cyano-based ylid formed in situ from the reaction between the corresponding phosphonium salt and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). The ylid formation is favored by the relatively high acidity of the methylenic protons of the phosphonium salt caused by the electron withdrawing strength of two cyano groups. Weaker bases, such as DBU, can be used to deprotonate the phosphonium salt and do not affect chemically the cyano and aldehyde groups, which are sensitive to strong base. The polymer was converted to all-*trans* configuration after iodine catalyzed isomerization. The dialdehyde monomer was produced by a Wittig-Horner reaction between mono-protected



Scheme 1.

terephthaldehyde and an aromatic diphosphonate ester bearing long alkoxy groups. The reaction has a high stereoselective orientation of the double bond. HPLC analysis showed that about 90% of the crude product had **E,E** configuration. Low amounts of **E,Z** and no **Z,Z** isomer were detected. The orange powder **E,E** isomer, was completely isolated from the yellow powder **E,Z** isomer after three crystallization steps from isopropanol.

3.2. Polymer structural and thermal characterization

GPC analysis showed a M_w of 3980 and a M_n of 3570. These low values can be attributed to the low reactivity of the cyano ylid. No peak impurities were observed in the low molecular weight region of the chromatogram. FTIR spectra shows terminal aldehyde group absorption at 1697 cm^{-1}, the cyano group absorption at 2226 cm^{-1}, and the characteristic absorption pattern of out-of-plane vibration of the all-*trans* double bonds at 912–964 cm^{-1} region. The ^{13}C and ^{1}H NMR spectra were consistent with the polymer structure. The aromatic region in both spectra is somewhat complex due to multiplicity of the peaks.

The first heating scan in DSC experiments of a non-annealed sample showed a clear-cut T_g at 44.6°C. The T_g could also be observed in the heating scan after quenching the sample with liquid nitrogen from 150°C. One weak exothermic transition was observed at 67.7°C in the first heating scan. This transition became weaker in the second cycle of heating and cooling steps from 0 to 150°C, and could not be observed in the cooling scans. Another large exothermic transition could be observed at 116.0°C, whose intensity slightly increased after cooling the sample from 125°C at a rate of 1°C/min and kept at 110°C for 6 h. This peak was assigned to the melting peak of the sample. The T_g and the middle peak could not be observed after the annealing process. The transitions observed indicate the polymer

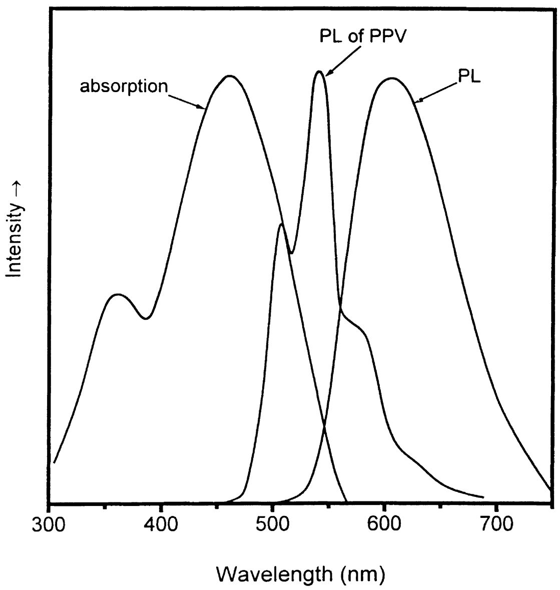


Fig. 1. Solid state absorption and PL for the CP. The PPV PL shows the possibility of energy transfer from PPV to CP.

has a semi-crystalline structure and may have the capability to develop mesomorphic order.

3.3. Absorption and photoluminescent properties

The solid state absorption and PL spectra of the CP are shown in Fig. 1. Both spectra were obtained from solid thin films spun onto quartz plates. The PL spectrum was acquired under 390 nm excitation wave length. The absorption spectrum showed two peaks centered at 358 and 460 nm. The band gap, i.e. the energy difference between HOMO and LUMO electronic states, can be estimated as 2.2 eV. The emission spectrum has a maximum at 612 nm. The orange fluorescence can be observed from polymer solutions in apolar solvents under natural light. The change of the band gap due to derivatization can be related to the electronic effects of the substituents on the polymer HOMO and LUMO levels [3]. There is a destabilization of the HOMO level by electron-donating groups and a stabilization of both HOMO and LUMO levels by the electron-withdrawing groups. When both are present in the same structure, the net result is a decrease of the energy of the LUMO level, while the energy of the HOMO level remains nearly the same. Hence, the presence of cyano and alkoxy groups generally produces red-shifted emitters [18]. However, the CP obtained in this study did not show a strong bathochromic emission. This can be explained by the fact that phenylene–vinylene units bearing cyano or alkoxy groups are interspersed by a nonsubstituted one. A pronounced bathochromic effect can be obtained when alkoxy and cyano groups belong to adjacent phenylene–vinylene units. This effect is associated with strong permanent dipoles associated with the $-OCH_3$ and $-CN$ groups [17] The separation of these groups decrease somewhat the interaction between them, producing a weaker permanent dipole. Thus, a less pronounced bathochromic effect is observed.

3.4. Electroluminescent properties of a single layer device

An ITO/CP/Ca device was built with a 80 nm thick emitter layer. The EL spectrum was obtained by applying a pulsed DC voltage forward bias. The use of a pulsed DC voltage instead a conventional one was desirable to maintain the integrity of the device during all measurements. The instability of the device was probably due to the low glass transition temperature of the polymer, decreasing somewhat the thermal and mechanical stability of the emission layer. The EL and PL spectra are similar and showed a maximum at 610 nm. The turn-on voltage was 8 V and the intensity of emission reached a maximum at 16 V giving rise to a luminance of about 800 cd/m^2. Under these conditions, the device could be left on for several hours with little luminance depletion.

3.5. Electroluminescence properties of double layer devices

An improvement of the emission properties was obtained from double layer devices of the type ITO/PPV/CP/Ca. Such devices turned on at 8 V with conventional DC forward bias. A maximum luminance of ca. 3000 cd/m^2 could be observed at 20 V applied voltage. The EL spectrum obtained from this device showed a slight blue shift in relation to the single layer architecture, which indicates only a slight contribution of PPV emission. The high emission efficiency of this device can be attributed to several factors. The most important contribution comes from a better balance of opposite charge injection and their combination near the interface of PPV and the CP layers. This effect is inherent to multilayer devices composed of PPV and a good electron transporting material such as cyano-modified polymers. The enhanced stability of the device is another advantage of the double layer structure as the PPV layer provides improved mechanical and thermal stability.

As is well known, PPV is not only a good hole transport material, but also a good emitter, in principle having PPV as hole transport layer in a device can affect the color of the emission by involving PPV in the overall emission process. This depends on the thickness of the PPV layer [25], the relative location of energy bands of PPV and the emitter layer [26] and the probability of electron transfer [27].The results shown in Fig. 2 indicate that in the present case the EL is mainly attributed to the CP and the PPV layer does not significantly contribute to the emission directly. As a result, a strong energy transfer process from PPV to the CP can be expected which is also supported by the large overlap between the emission of PPV and the absorption of the CP (Fig. 1). In principle, EL processes involved in a double layer device (anode/PPV/emitter/cathode) may include the following:

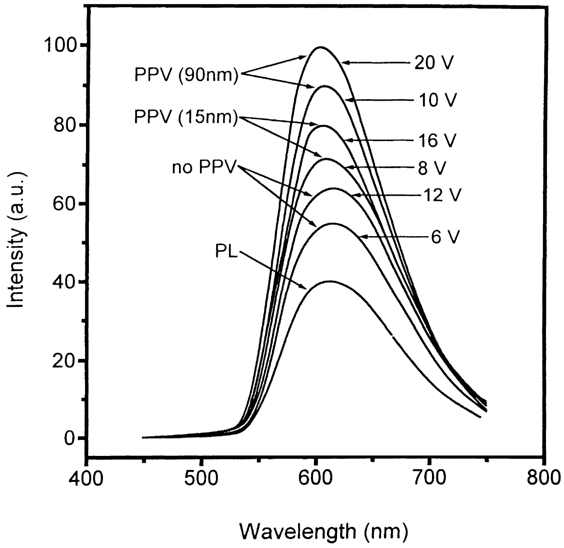


Fig. 2. EL of CP for single and double layer devices with variation in PPV thickness and voltage.

1. Injected holes and electrons recombine to form excitons in both the PPV and the emitter layer near the interface. The excitonic energy in the PPV layer will be transferred to the emitter layer, which gives rise to a single emission.
2. Injected carriers recombine to form excitons in both the PPV and emitter layers. These excitons decay independently in both layers, which produces a mixed emission spectrum.
3. Injected carriers recombine to form an interfacial complex at the interface between the PPV and the emitter layer. The interfacial excitons radiatively decay, which is responsible for an emitted color distinct from both PPV and the emitter layer.
4. The results of the very slightly blue shifted EL from ITO/PPV/CP/Ca compared to the single layer device ITO/CP/Ca clearly favors the proposed process (1).

We also note that increasing the thickness of the PPV layer increases the probability of excitons formed in the bulk that cannot migrate to the CP layer. The radiative decay of a fraction of these excitons will produce light that will be emitted from the device from the PPV layer and the observed emission will therefore tend to blue shift with increasing thickness (from 15 to 90 nm) as can be seen in Fig. 2. Changing the thickness of the PPV layer will also affect charge injection into the device. A thicker PPV layer requires a higher voltage for a given EL intensity, a thinner PPV layer facilitates hole injection from the anode because the energy bands of the PPV layer are tilted further due to the accumulated space charge at the interface, which results in a EL intensity more sensitive to the voltage change (Fig. 3). The detailed effects of the thickness of PPV layer are currently under investigation.

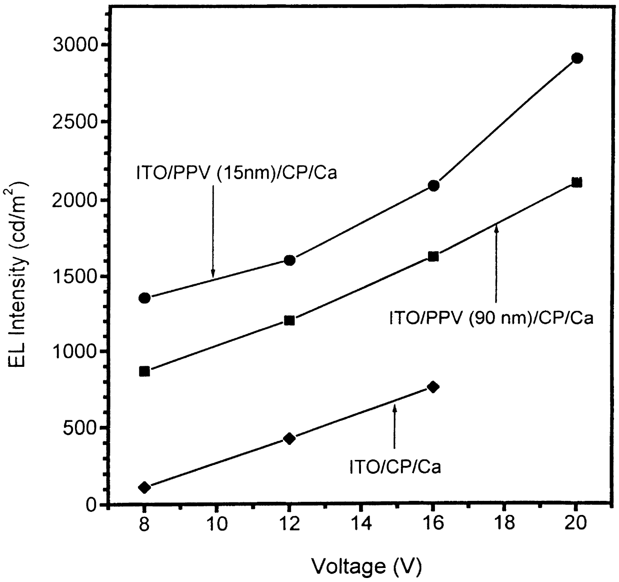


Fig. 3. Comparison in brightness for single and double layer LEDs.

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References

[1] Friend RH, Greenham NC. Electroluminescence in Conjugated Polymers. In: Skotheim TA, Elsenbaumer RL, Reynolds JR, editors. Handbook of conducting polymers, New York: Marcel Dekker, 1998.
[2] Baigent DR, Greenham NC, Grüner J, Marks RN, Friend RH, Moratti SC, Holmes AB. Synth Met 1994;67:3.
[3] Cornil J, Beljonne D, dos Santos DA, Brédas JL. Synth Met 1996;76:101.
[4] Cornil J, Beljonne D, dos Santos DA, Shuai Z, Brédas JL. Synth Met 1996;78:209.
[5] Moratti SC, Cervini R, Holmes AB, Baigent DR, Friend RH, Greenham NC, Grüner J, Hamer; PL. Synth Met 1995;71:2117–20.
[6] Greenham NC, Friend RH, Bradley DDC. Adv Mater 1994;6:491.
[7] Zhang C, Hoger S, Pakbaz K, Wuld F, Heeger AJ. J Electron Mater 1993;22:413.
[8] Braun D, Heeger AJ. Appl Phys Lett 1991;58:1982.
[9] Conwell E. Trends Polym Sci 1997;5:218.
[10] Andersson MR, Yu G, Heeger AJ. Synth Met 1997;85:1275.
[11] Samuel ID, Rumbles G, Collison CJ. Phys Rev 52B 1995;16:R11 573.
[12] Denton FR, Sarker A, Lahti PM, Garay RO, Karasz FE. J Polym Sci A: Polym Chem 1992;30:2233.
[13] Lahti PM, Sarker A, Garay RO, Lenz RW, Karasz FE. Polymer 1994;35:1312–6.
[14] Kim KD, Park JS, Kim HK, Lee YB, No KT. Macromolecules 1998;31:7267.
[15] Staring EGJ, Demandt RCJE, Braun D, Rikken GLJ, Kessener YARR, Venhuizen AHJ, Knippenberg MMF, Bouwmans M. Synth Met 1995;71:2179–80.
[16] Gill RE, Hilberer A, van Hutten PF, Berentschot G, Werts MPL,

Meetsman A, Wittmann JC, Hadziioannou G. Synth Met 1996;84:637.
[17] Pinto MR, Hu B, Karasz FE, Akcelrud L. Polymer 2000;41:2603.
[18] Graham NC, Moratti SC, Bradley DDC, Friend RH, Holmes AB. Nature 1993;365:628–9.
[19] Brouwer HJ, Hilberer A, Krasnikov VV, Wertz M, Wilderman J, Hadziioannou G. Synth Met 1997;84:881.
[20] Dottinger SE, Hohloch M, Hohnholz D, Segura JL, Steinhuber E, Hanack M. Synth Met 1997;84:267.
[21] Hanack M, Hohloch M, Segura JL, Dottinger SE, Hohnholz D, Steinhuber E, Spreitzer H. Synth Met 1997;84:319.
[22] Kim JJ, Kang SW, Hwang DH, Shim HK. Synth Met 1993;57:12.
[23] Greenwald Y, Xu X, Fourmigue M, Srdanov G, Koss C, Wudl F, Heeger AJ. J Polym Sci A: Polym Chem 1998;36:3115.
[24] Syper L, Mlochowski J, Klock K. Tetrahedron 1983;39:781.
[25] Hu B, Karasz FE. Chem Phys 1998;227:263.
[26] Suzuki H, Hoshino S. J Appl Phys 1996;79:88.
[27] Hu B, Zhang N, Karasz FE. J Appl Phys 1998;83:881.