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Heterocycle-substituted poly(*p*-phenylene vinylene) for light-emitting devices

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Abstract

Results are presented which explore the synthesis, characterization and electroluminescence performance of a new type of conjugated polymer, poly(2,5-diphenyl-1,3,4-oxadiazolyl)-4,4′-vinylene (O–PPV). A light-emitting diode consisting of ITO/O–PPV/Al is driven at about 6 V and has a peak emission wavelength of 483 nm, and this is in agreement with the result determined by the X-ray photoelectron spectroscopy (XPS) technique. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

Over the course of the past six years there has been increasing interest in applications of polymeric materials in light-emitting devices, and there is a strong possibility that these materials will find commercial use in a variety of display applications since a light-emitting diode (LED) with poly(*p*-phenylene vinylene) (PPV) as the active layer was first reported in 1990 [1]. The perceived advantages of these materials lie in their ability to be used in ways that complement the use of traditional inorganic semiconductors. For instance, polymer LEDs can be made on flexible substrates, and large areas are accessible via low cost film deposition. Moreover, chemical tuning of the polymer electronic structure potentially allows access to the whole visible spectrum. Colours available already include red, green and blue, required for full colour displays [2–4]. Controlling the conjugation length by introducing non-conjugated segments in the main chain of conjugated polymers is an effective way of obtaining blue light emission [5]. The introduction of non-conjugated segments not only results in the confinement of electrons in conjugated parts, but also reduces polymer aggregation, thereby improving luminescent efficiency [6].

In the course of our studies on synthetic routes to poly-(2,5-diphenyl-1,3,4-oxadiazolyl)-4,4′-vinylene (O-PPV), we successfully introduced the electron-withdrawing oxadiazole unit in the main chain of PPV. For comparison, an (ITO/PPV/Al) diode will emit yellow–green radiation, whereas the device (ITO/O-PPV/Al) described here emitted blue light.

2. Experimental

IR spectra were recorded on a Nicolet 5DX FT-IR spectrometer, ^{1}H NMR were recorded with a Varian Unity Plus-400 spectrometer, photoelectron spectra were recorded using a Perkin-Elmer PHI1600 ESCA system, and fluorescence spectra were obtained on a Hitachi-4000. Polymer intermediates, compounds **1** and **2** shown in Scheme 1, were respectively prepared using a modified literature procedure [7] and according to a previously reported synthetic method [8].

2.1. Preparation of monomer salt 3

To a stirring MeOH solution (100 ml) of the bromomethyl compound **2** (8.16 g, 20 mmol) was added 10 ml of dimethyl sulfide. The reaction mixture was then heated under reflux for 4 h. The solvent and excess dimethyl sulfide were distilled off and the white solid of monomer salt was precipitated by adding 200 ml acetone. The solid was recrystallized twice

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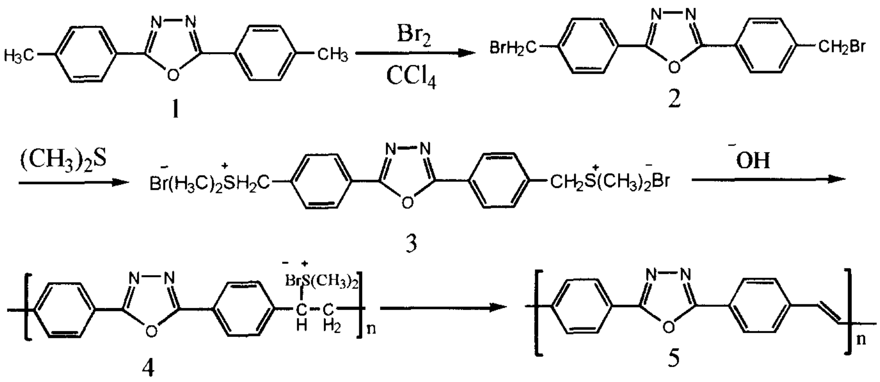


Scheme 1.

from a mixture of methanol and acetone (1:1) to yield colourless crystals (7.7 g, 72.3%); m.p. 224–226°C. ^{1}H NMR (D_2O, 400 MHz) δ: 7.6, 8.1 (4H, s, phenyl), 4.5 (4H, s, CH_2–S), 2.8 (12H, s, S–CH_3). *Anal.* Calc. for $C_{20}H_{24}Br_2N_2OS_2$: C, 45.11; H, 4.51; N, 5.26; S, 12.03. Found: C, 45.13; H, 4.48; N, 5.25; S, 12.03%.

2.2. Preparation of polymers 4 and 5

A thoroughly degassed and stirred solution (50 mmol in 10 ml MeOH) of the monomer salt **3** maintained at −10 to −5°C was treated with 50 mmol (2 ml, maintained at −5 °C) of NaOH in MeOH. The reaction mixture became viscous and a thick gel was obtained in 4 h, then quenched by neutralization with 0.5 M HCl. The gel was dialysed in MeOH containing 1% water for 3 days until bromide ions were no longer detected by addition of silver nitrate to the solution. Allowing slow evaporation at room temperature, the solution of the polymer precursor **4** gave films, and the films were converted to the desired polymer **5** by heating to 200°C under nitrogen for 3 h. *Anal.* Calc. for $C_{16}H_{10}N_2O$: C, 78.05; H, 4.07; N, 11.38; S, 0. Found: C, 78.10; H, 4.03; N, 11.37; S, 0.12%.

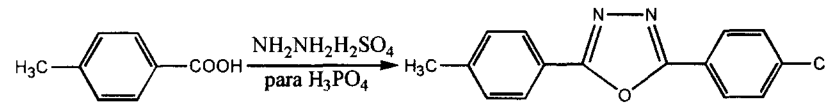
2.3. LED device preparation

Indium–tin oxide (ITO)-coated glass (30 Ω/□) was used as the positive electrode, a layer of polymer precursor **4** was then deposited by spin-coating, and thermally converted to about an 80 nm thick heterocycle-substituted PPV film, and finally Al was evaporated onto the polymer.

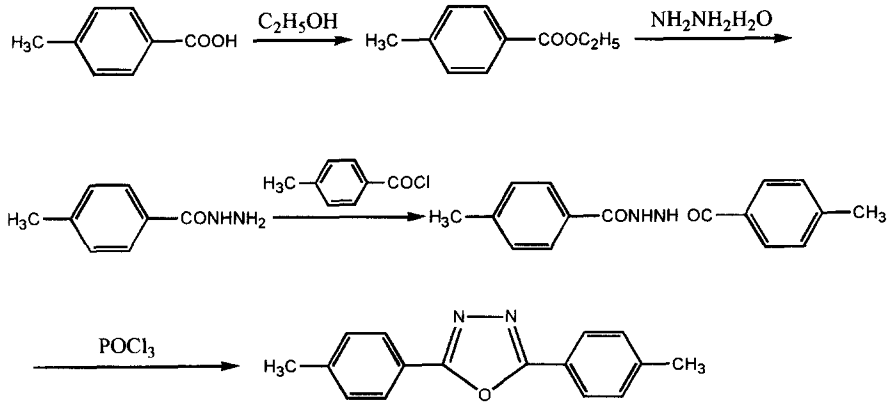
3. Results and discussion

3.1. Synthesis

The synthesis of compound **1** was achieved following Schemes 2 and 3. The yield of compound **1** in Scheme 2 was 92.0%, but the total yield in Scheme 3 was about 39.4%. Apparently, the results of Scheme 2 were much more promising than that of Scheme 3 used before [7].



Scheme 2.



Scheme 3.

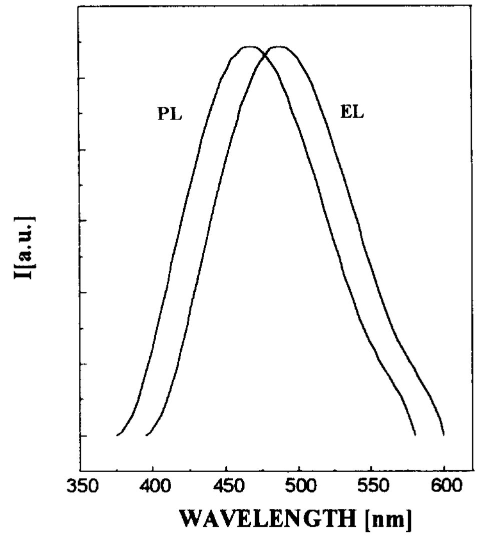


Fig. 1. EL and PL spectra of a device with an ITO/O–PPV/Al structure.

An IR spectrum of the O–PPV compound showed an absorption peak at 962 cm^{-1}, as expected for *trans*-vinylene. Additionally, elemental analysis of the polymer showed the presence of very little sulfur in the fully conjugated polymer.

3.2. Optical characterization

From the Fig. 1 we know that the device (ITO/O–PPV/Al) fabricated with the novel polymer of heterocycle-substituted PPV emitted blue light (λ_{max} = 483 nm), while the LED constructed using PPV (ITO/PPV/Al) emitted yellow light. The most likely explanation of the difference is that a decrease in the conjugation length of the heterocycle-substituted PPV increases the bandgap to values higher than that of PPV, resulting in a blue shift in the emission spectrum. Karasz and co-workers [9] reported that the energy bandgap of PPV by the X-ray photoelectron spectroscopy (XPS) technique is about 3 eV and the VEH bandgap of PPV calculated by Fablman et al. [10] is about 2.3 eV. Fig. 2 shows that the energy bandgap of O–PPV by the XPS technique is about 4 eV, which is higher than that of PPV. This is in agreement with the luminescence results.

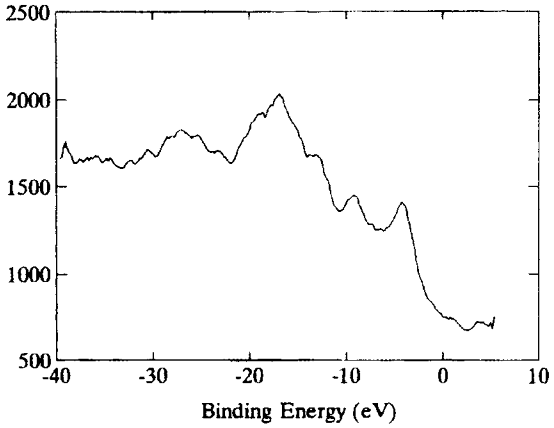


Fig. 2. XPS spectrum of O–PPV.

4. Conclusions

A novel polymer, poly(2,5-diphenyl-1,3,4-oxadiazolyl)-4,4′-vinylene (O–PPV) was synthesized starting from compound **1**. Unlike the yellow light from the device of ITO/PPV/Al, the device of ITO/O–PPV/Al fabricated with the novel polymer emitted blue light. The photoluminescence and XPS results are in agreement.

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