

A novel green light-emitting material containing both hole and electron transporting units

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Organic light-emitting polymers have been the subject of intensive investigations because their luminescent properties may be fine tuned by manipulating their chemical structures and ease spin-coating and printing process. For most conjugated polymers, the injection and the transportation of electrons are much difficult than those of holes [1]. Many of these polymers were combined with suitable charge-transporting layers to increase their efficiency [2, 3]. Therefore, luminescent polymers with balanced charge injection and transport are very important. Conjugated polymers with high electron affinities have been found to show good electron transporting abilities. Such polymers usually contain electron-withdrawing groups as substituents, which lower the conduction band of the polymers, to enhance electron injection and transport. Electron deficient oxadiazole units have been found to be efficient in promoting electron transport property when incorporated into PPV main chain or as substituents [4, 5]. The triphenyl amine and its derivatives are known as the hole transporting materials. And they are typically used for the construction of heterojunction multi-layer OLED. To our best knowledge, multifunctional molecules containing three components—triphenylamine, oxadiazole and distyryl benzene fused together have not been described in the literatures.

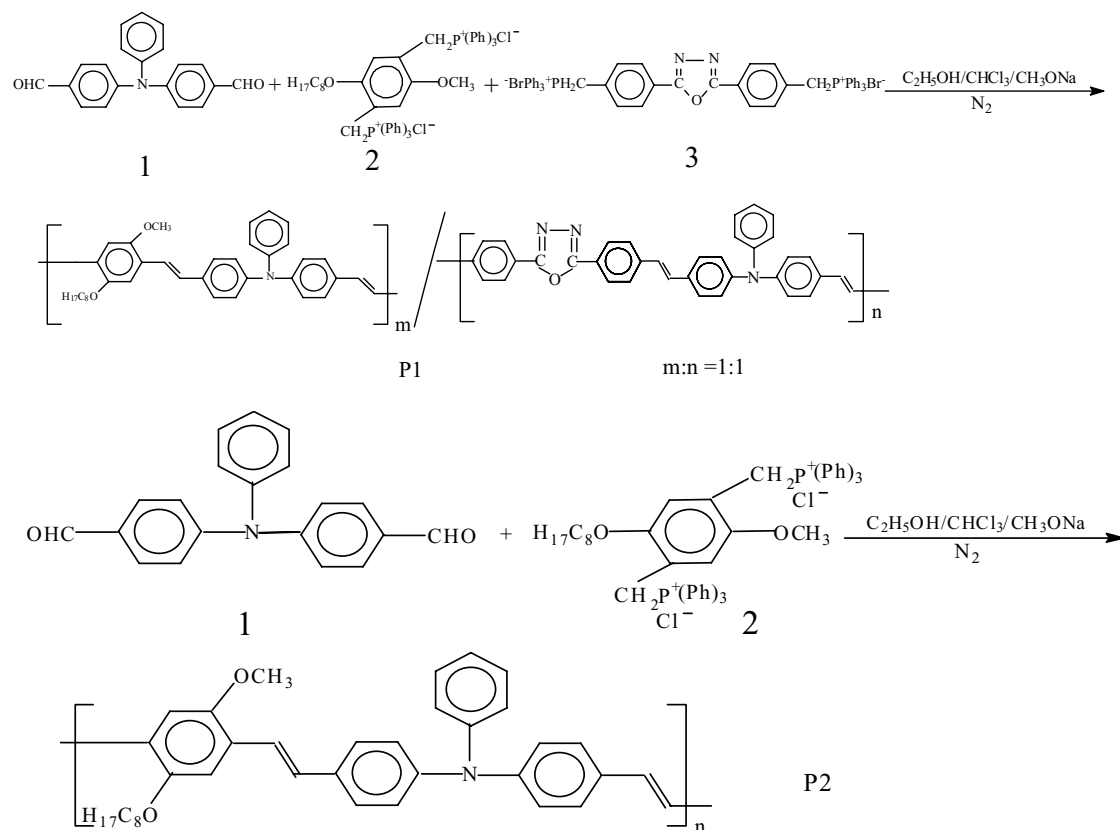
Here we report a new conjugated multifunctional polymer (P1) with the triphenyl amine, 1,3,4-oxadiazole and distyryl benzene chromophores in order to increase the electron mobility and get the balanced injection ability. The monomers and polymers were characterized and the physical properties such as thermal and optical properties were studied as well. Meanwhile, the synthesis of poly(triphenylamine-alt-2-methoxy-5-octoxy-1,4-phenylene vinylene) (P2) is chosen for comparison, the oxadiazole group's effect on the polymer optical properties was investigated. Their chemical structures and the synthetic route are shown in Scheme 1.

4,4'-Diformaltriphenylamine (1) was synthesized by Vilsmeier reaction. In order to synthesize bis-formyl-triphenylamine in a high yield, we used the procedure by varying the molar ratio of DMF and POCl₃. 2-Methoxy-5-octoxyl-1,4-xylenebis (triphenyl phosphonium chloride) (2) was synthesized in three steps from 4-methoxyphenol in 91% yield by etherification followed by conversion to the chloromethylation and

thereafter conversion to the triphenylphosphonium salt (2). 5-Bis(4-tolylene-triphenylphosphonium bromide)-1,3,4-oxadiazole (3) was prepared by the *p*-toluic acid as the starting material, then to bromomethylation and followed by conversion to the triphenylphosphonium salt. Polymerization was carried out by a Wittig condensation at room temperature using sodium methoxide in 1:1 (v/v) ethanol/chloroform mixing solvent. The polymers were isolated by filtration and were purified by precipitation from chloroform to methanol several times. After drying in the vacuum oven at room temperature, the polymers were typically obtained in 60–70% yields. The polymer P1 was a brown red powder and was soluble in the conventional solvents, such as tetrahydrofuran, toluene and chloroform. FT-IR spectra (Fig. 1) show a drastic decrease in the intensity of the aldehyde carbonyl band and the appearance of olefinic C–H stretching band at 1690 and 963 cm⁻¹ in the P1 and P2 as compared with the dialdehyde comonomer. Meanwhile, a strong C=N stretching band at 1591 cm⁻¹ exists in the polymer P1, and the molecule structures of copolymers P1 and P2 were also confirmed from the ¹H-NMR spectra. The ¹H-NMR signals in the olefinic regions appear at δ of about 7.1–7.7 ppm, typical for trans stilbene moieties, and also δ at about 6.6–6.8 ppm, attributable to the cis isomer. The weight-average molecular weight (M_w) of P1 was measured by gel permeation chromatography (GPC) with polystyrene as standards and THF as the eluant, M_w was about 4100 and the polydispersity index (PDI) was 1.8, M_w for P2 was about 3500, PDI was 1.53.

The thermal stability of conjugated polymer is an important factor for obtaining stable EL devices. None of copolymer P1 and P2 showed a crystallization phase and melting point, which can form desirable stable amorphous phases in a deposited film. The thermal stability of the polymers was evaluated through TGA as shown in Fig. 2. Glass transition temperature (T_g) of the polymers was examined using differential scanning calorimetry (DSC) between 20 and 300 °C with a heating rate of 10 K/min. The DSC measurement displayed that a glass transition temperature of P1 was 119 °C, which was much higher than 72 °C of P2. According to the thermogravimetric analysis (TGA), the copolymer P1 was stable upto 423 °C in nitrogen atmosphere at 5% weight loss which was much higher than 218 °C of P2. This indicates that the incorporation of the oxadiazole

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Scheme 1

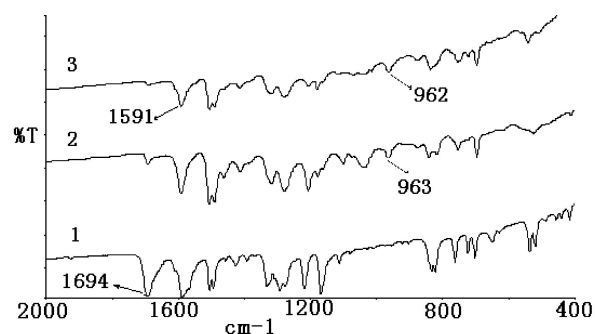


Figure 1 FT-IR spectra of (1) 4,4'-diformaltriphenylamine (monomer 1), (2) P2 and (3) P3.

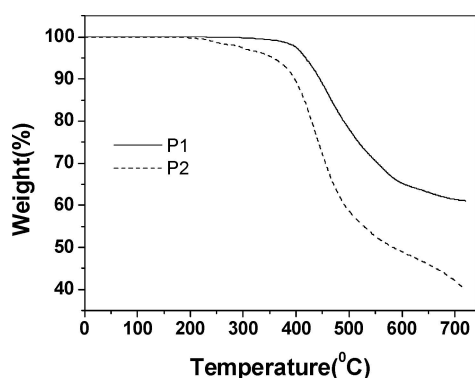


Figure 2 TGA thermograms of P1 and P2.

group stiffens the main chain and the copolymer P1 possesses better thermal stability.

UV-Vis spectra were measured with a Lambda 25 UV-Vis spectrophotometer. The fluorescence spectrum

measurements were conducted on a Perkin-elmer LS55 spectrophotometer with a xenon lamp as light source. The UV-Vis absorption and emission spectra of the polymers dissolved in chloroform solution and solid film state are shown in Figs 3 and 4. The optical data are listed in Table I. The maximum absorption wavelength (433 nm) of P2 was red-shifted relative to that

TABLE I Optical data of the polymers in solution and film

Polymers	Solution		Film	
	Abs (nm)	Em (nm)	Abs (nm)	Em (nm)
P1	423	507	446	533
P2	433	505	466	517

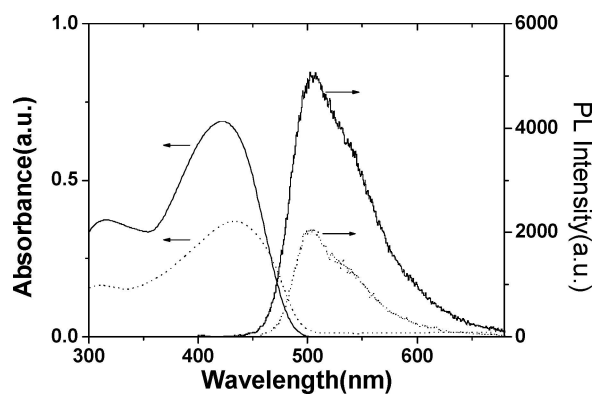


Figure 3 Optical absorption and photoluminescence (PL) spectra of P1 (solid line) and the P2 (dashed line) in CHCl_3 solutions (ca. 1×10^{-2} g/dL).

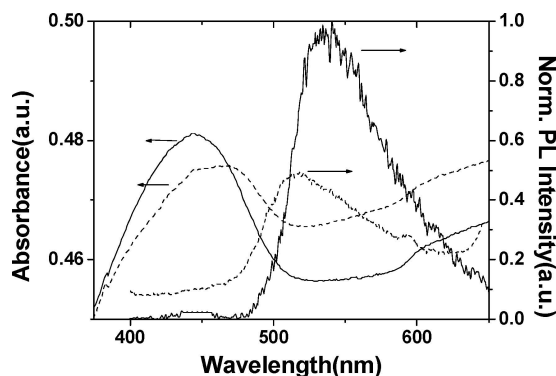


Figure 4 Optical absorption and photoluminescence (PL) spectra of P1 (solid line) and P2 (dashed line) in the film on a glass plate.

(423 nm) of P1 because the oxadiazole group introduced to the main chain and decreased the conjugation length. As shown in Fig. 4, a spin-casting film of the two copolymers onto the glass plate, the absorption maxima (λ_{\max}) locate at 446 and 466 nm, respectively, for P1 and P2. Interestingly, the emission spectra of the two copolymers in the solution are similar in shape, but the emission intensity of P1 is much stronger than that of P2 in the same concentration, which shows that the oxadiazole group can absorb energy and transfer it to the main chain, thus leading to the enhanced emitting light of the main chain. P1 exhibits broader peak shape in the solid state compared to that of P1 in the solution, which may be caused by the different and more excited states in the film. The emission peak of P1 in the solid film locates 533 nm, it has red-shifted 16 nm compared to that of P2.

As shown in Fig. 5, in a wide range, from 1×10^{-3} to 1×10^{-1} g/dL, the emission intensity of P1 increases with the concentration increasing. That means the concentration quenching did not happen for the polymer in the concentration region.

The matches of HOMO, i.e. the highest occupied molecule orbital, and LUMO, i.e. the lowest unoccupied molecular orbital, with work functions of electrodes are very important to LED device. Usually the HOMO and the LUMO are measured directly by electrochemical cyclic voltammetry (CA). The onset potentials of the oxidation and reduction processes of a material have a correlation to the ionization potential (IP, be equal to HOMO) and electron affinity (EA, be equal to

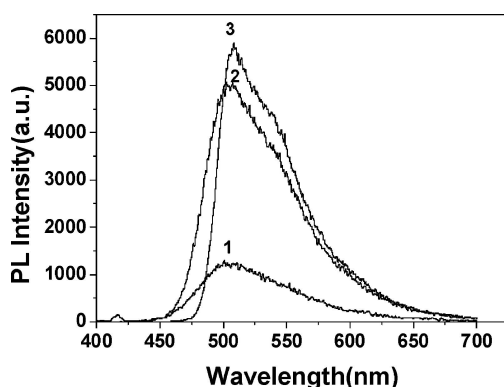


Figure 5 Photoluminescence spectra of P1 in different concentrations chloroform solution (g/dL): (1) 1×10^{-3} ; (2) 1×10^{-2} ; (3) 1×10^{-1} .

LUMO). When Ag/AgCl electrode is used as the reference electrode, the correlation can be expressed as [6]:

$$E_{\text{HOMO}} = -|\text{IP}| = -|eE_{\text{ox}} + 4.37|$$

$$E_{\text{LUMO}} = -|\text{EA}| = -|eE_{\text{red}} + 4.37|$$

$$E_{\text{g}} = |\text{IP}| - |\text{EA}| = E_{\text{LUMO}} - E_{\text{HOMO}}$$

E_{ox} and E_{red} are onset potentials of the oxidation and reduction process, respectively. For P1, the onset potential of oxidation occurs at 1.0 eV, so the value of HOMO is calculated as -5.37 eV. The band gap (E_{g}) is estimated as 2.43 eV from the UV-Vis absorption spectrum. The value of LUMO is calculated as -2.94 eV. As for P2, the onset of oxidation occurs at 0.58 eV, so the value of HOMO is -4.95 eV. E_{g} is estimated as 2.44 eV from the UV-Vis edge absorption, the value of LUMO is -2.51 eV. To a single-layer LED device of ITO/P1 (or P2)/Al, the energy barriers for electron and hole injection are 1.36 and 0.67 eV, respectively, for P1 and the energy barriers for P2 are 1.79 and 0.25 eV. It means that P1 possesses a better balanced injection and better electron injection capability because of oxadiazole unit in the configuration than that of P2. Such information is beneficial to the device design.

In summary, a new conjugated multifunctional polymer (P1) containing the triphenyl amine, 1,3,4-oxadiazole and distyryl benzene chromophores was prepared using the Wittig polycondensation reaction. The resulting polymer can dissolve in the common solvents and spin-castability from a solution. In spite of the oligomeric molecular weight of the polymer, P1 showed higher thermal stability than that of P2. The polymer showed blueish green photoluminescence with the maximum at 507 and 533 nm in a CHCl_3 solution and in a film, respectively. In a wide range, from 1×10^{-3} to 1×10^{-1} g/dL, the emission intensity of P1 increases with the concentration increasing. The electrochemical studies suggested that P1 has better balanced injection ability than that of P2 because of the oxadiazole group. Electroluminescent property of the polymer is under investigation.

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