

Novel Bipolar Conjugated Polymer Containing Both Triphenylamine and Oxadiazole Units

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Abstract: A novel bipolar conjugated polymer containing triphenylamine and 1, 3, 4-oxadiazole units was synthesized by Suzuki reaction. Its structure and properties were characterized by NMR, IR, UV-Vis, PL spectroscopy and electrochemical measurement. The photoluminescent spectroscopy and cyclic voltammograms measurement demonstrated that the resulting polymer shows blue emission (477 nm) and possesses both electron and hole-transporting property.

Keywords: Light-emitting polymer, bipolar conjugated polymer, triphenylamine-containing polymer, oxadiazole-containing polymer.

In the past decade, conjugated polymers have received considerable attention because of their promising applications in opto-electronic devices¹. In particular, significant progress has been achieved in the development of light-emitting diodes (LEDs) based on the conjugated polymers²⁻³. However, for most of the conjugated polymers, hole injection/transport is more favorable than electron injection/transport, which leads to the unbalancement of electron and hole injection. For achieving high efficient PLED device, it is desirable to design and synthesize the bipolar conjugated polymer with both electron and hole transporting abilities for the fabrication of single-layer PLED⁴⁻⁵.

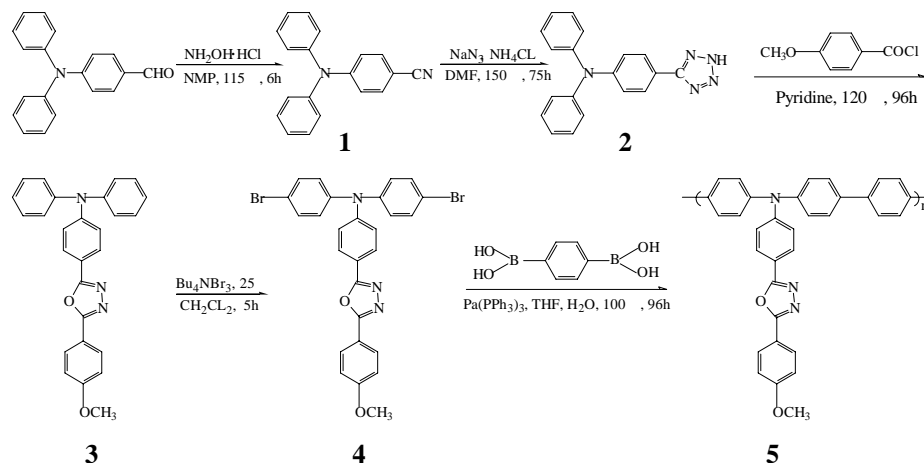
In this letter, we present the synthesis and preliminary properties of the new blue light-emitting polymer containing both triphenylamine and 1, 3, 4-oxadiazole units, for achieving blue-emitting polymer with both electron and hole transporting abilities. The idea of design is that the aromatic substituted triphenylamine derivatives are promised candidates both as blue light-emitting substance and hole-transporting materials⁶, and the 1, 3, 4-oxadiazole derivatives have been widely used both as blue light-emitting substance and electrons transporting materials⁷.

Synthesis and characterization

The synthetic routes for novel bipolar conjugated polymer associated with triphenylamine analogue as the main chain and 1, 3, 4-oxadiazole moiety as the side chain

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are outlined as follows:



Compound 1: A solution of *N,N*-diphenylaminobenzaldehyde (11.3 g, 41 mmol) and hydroxylamine hydrochloride (6.9 g, 100 mmol) in 40 mL purified *N*-methylpyrrolidone was heated at 115°C under a nitrogen atmosphere for 6 h. After cooling to room temperature, the crude product was poured into water, and then extracted with CHCl_3 . The CHCl_3 solution was washed with brine, dried (Na_2SO_4) and then the solvent was removed. The crude product was recrystallized (EtOH) to afford the pure nitrile 10.2 g (yield 90%). mp 125.8-126.5°C. ^1H NMR (d_1 - CDCl_3 , δ ppm): 6.94-6.99 (d, 2H, $J=8.8$ Hz), 7.12-7.20 (m, 6H), 7.30-7.37 (m, 4H), 7.39-7.44 (d, 2H, $J=8.8$ Hz).

Compound 2: A mixture of 4-cyanotriphenylamine (10 g, 37 mmol), sodium azide (37.5 g, 590 mmol) and ammonium chloride (32 g, 590 mmol) in 150 mL of dried DMF was stirred and heated under reflux for 75 h. Then the cooled solution was added to aqueous hydrochloric acid. The precipitate was collected and washed with water. Recrystallization from toluene gave the desired product **2** 10.1 g (yield 90%). mp 216-217°C. ^1H NMR (d_1 - CDCl_3 , δ ppm): 7.88-7.92 (d, 2H, $J=8.4$ Hz), 7.24-7.34 (m, 4H), 7.04-7.16 (m, 9H).

Compound 3: A solution of 4-tetrazolyltriphenylamine (9 g, 30 mmol) and *p*-methoxybenzoyl chloride (5.6 g, 33 mmol) in 50 mL dried pyridine was heated under reflux for 96 h. After cooling to room temperature, extracted with CHCl_3 . The CHCl_3 solution was washed with brine, dried (Na_2SO_4) and the solvent was removed by evaporation. The crude product was purified by column chromatography (eluent: acetic ether/petroleum ether 1:1 v/v) to afford the pure product **3** 9.2 g (yield 73%). mp 134°C. ^1H NMR (d_1 - CDCl_3 , δ ppm): 3.87 (s, 3H), 7.01-7.03 (d, 2H, $J=8.8$ Hz), 7.09-7.17 (m, 8H), 7.30-7.34 (m, 4H), 7.91-7.93 (d, 2H, $J=8.8$ Hz), 8.03-8.06 (d, 2H, $J=8.8$ Hz).

Monomer 4: A solution of compound **3** (4.2 g, 10 mmol) in 10 mL CH_2Cl_2 at 25°C was added a solution of Bu_4NBr_3 (9.6 g, 20 mmol) in 10 mL CH_2Cl_2 . The reaction mixture was stirred for 5 h. The organic layer was washed with a solution of sodium hydrogen sulfite twice and dried over Na_2SO_4 , the solvent was removed by evaporation. The crude product was purified by recrystallization (acetic ether) to afford the pure

product **4** 5.5 g (yield 95%). mp 172°C. ^1H NMR ($\text{d}_1\text{-CDCl}_3$, δ ppm): 3.88 (s, 3H), 7.00-7.04 (m, 5H), 7.09-7.15 (m, 4H), 7.31-7.43 (m, 3H), 7.93-7.95 (m, 2H), 8.04-8.06 (d, 2H, $J=8.4$ Hz). Anal Br: calcd. 27.73; found, 27.79 %.

Polymer 5: The polymerization was carried out through palladium-catalyzed Suzuki condensation reaction between monomer **4** and *p*-dibromobenzene in the presence of K_2CO_3 . The typical polymerization condition is as follows: The mixture of monomer **4** (0.577 g, 1 mmol), *p*-dibromobenzene (0.166 g, 1 mmol), $(\text{PPh}_3)_3\text{Pa}$ (25 mg) and K_2CO_3 (0.8 g) in 10 mL of THF and 3 mL of water was refluxed for 4 days. After cooling to room temperature, the resulting mixture was extracted with CHCl_3 and washed with 1 mol/L HCl and water. 0.53 g polymer **5** was obtained in 71% yield by precipitation in methanol twice.

The resulting polymer **5** has good solubility in common organic solvents such as THF, CHCl_3 and CH_2Cl_2 . Its average molecular weight was determined to be about 7680, by gel permeation chromatogram (GPC) with polystyrenes as standard and THF as eluent. A combination of ^1H -NMR, ^{13}C -NMR, FT-IR and elemental analysis confirms the formation of polymer **5**. This polymer possesses a glass transition temperature (T_g) of 124°C by differential scanning calorimetry (DSC) and good thermal stability.

Electrochemical and optical properties

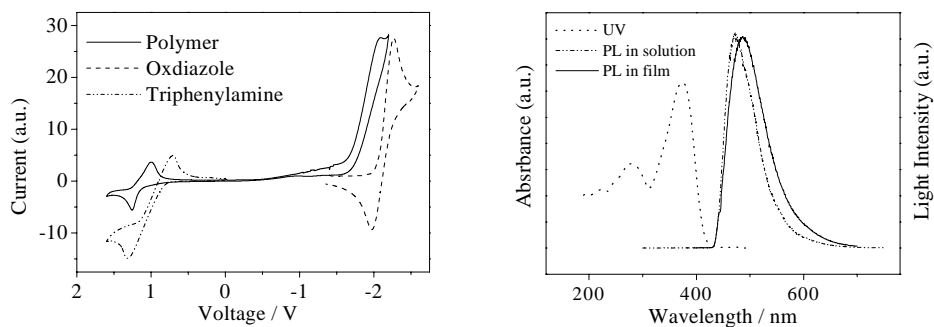
Figure 1 shows the cyclic voltammograms of polymer **5**, triphenylamine and 2, 5-diphenyl-1, 3, 4-oxadiazole. Cyclic voltammetry (CV) measurement was performed with a three-electrode electrochemical cell in 0.1 mol/L tetrabutylammonium perchlorate solution in acetonitrile at room temperature, using the platinum as counter electrode and Ag/AgCl as reference electrode. The resulting polymer exhibits a reversible and a quasi-reversible redox process for anodic and cathodic range, respectively. Comparing with the CV behavior of triphenylamine and 2, 5-diphenyl-1, 3, 4-oxadiazole, the oxidation and reduction peaks appeared in polymer **5** can be attributed to the redox feature of triphenylamine moiety and 2, 5-diphenyl-1, 3, 4-oxadiazole unit, indicating that the resulting polymer **5** possesses the corresponding hole-transporting and electron transporting property. The onset potentials of oxidation and reduction are 1.05 V and -1.60 V, respectively. Therefore, its E_{HOMO} is estimated to be -5.85 eV and E_{LUMO} is to be -3.2 eV. The optical band gap energy, E_g , is calculated to be 2.65 eV ($E_{\text{HOMO}} - E_{\text{LUMO}}$).

Figure 2 shows UV-Vis and photoluminescent spectra of polymer **5**. Two absorption peaks appear at 278 and 375 nm, which can be attributed to $\pi\text{-}\pi^*$ transition of the oxadiazole moiety and the main chain of conjugated polymer. From the onset wavelength (431 nm), its band gap, E_g , is estimated to be 2.88 eV. This result is consistent with that determined by cyclic voltammetry measurement.

The Polymer **5** can emit intensive blue fluorescence in film or in solution under the irradiation of UV light. It can be seen from **Figure 2** that its photoluminescent spectra exhibit a maximum at 477 (in solution) and 486 nm (in film), respectively, corresponding to blue light emission. From the above discussion, we can conclude that the resulting polymer is a promising candidate for blue-emitting single-layer polymer devices. The

electroluminescent study using this polymer as emitting material is under investigation.

Figure 1 Cyclic voltammogram of polymer **5**, **Figure 2** PL of polymer **5** in CHCl_3 and in oxadiazole and triphenylamine in CH_3CN film, UV spectrum of polymer **5** in CHCl_3



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