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Synthesis and properties of new electroluminescent polymers possessing both hole and electron-transporting units in the main chain

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Abstract

New EL polymers possessing both hole and electron-transporting units in the main chain are synthesized. The polymer prepared by palladium catalyzed Heck reaction of **10** and **15** show a large weight average molecular weight (M_w) (25,000) and small polydispersity index (PDI) (1.2). The oligomers synthesized by Wittig condensation have M_w of 4000 and PDI of 1.8. All the polymer and oligomers synthesized exhibit remarkable thermal stability with high decomposition temperature and high T_g as determined by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) under nitrogen atmosphere. The EL emission maximum peaks of the materials prepared are in the range of 535–560 nm corresponding to green–yellowish-green. Among the three electron-transporting moieties, the 1,3,4-oxadiazole unit shows the best electron injection and transporting property.

Keywords: Electroluminescent; Electron-transporting; Hole-transporting

1. Introduction

Since the first report in 1990 on the electroluminescence (EL) of polymers [1], a large number of polymers have been synthesized and investigated because of their potential applications in the next generation full color flat panel displays [2–4].

There are, however, many problems to be solved for polymeric EL devices such as poor durability and low thermal stability. In addition, there still remain problems associated with inefficient charge injection into the polymer layer despite of the considerable progress in improving the efficiency of three-layered (electrode/polymer/electrode) devices. The use of a molecular charge-transporting layer between the light-emitting material and the corresponding electrode improved the device performance considerably [5–7]. Although multilayer light-emitting diodes (LEDs) show high efficiency and long life-time, they involve complex and difficult processes in fabrication. It is, therefore, desirable to design and synthesize a bifunctional polymer that possesses both a hole-transporting unit and electron-affinitive/hole-blocking unit in the main chain in order to promote the charge-transporting and to simplify the fabrication process [8–11].

Triphenylamine (TPA) has been the most widely used hole-transporting material [12,13] while oxadiazole, triazine and triazole have been used as the electron-transporting or hole-blocking material in the organic LEDs [14–16]. We synthesized bifunctional polymer and oligomers possessing both hole and electron-transporting units, i.e. TPA and oxadiazole (OXA–TPA), TPA and triazine (TZN–TPA), or TPA and triazole (PTZL–TPA) in the main chain and investigated EL properties of the materials prepared.

2. Experimental section

2.1. Instruments

^{1}H (300 MHz), ^{13}C (100.6 MHz) NMR spectra were recorded using $CDCl_3$ and DMSO-d_6 solvent unless otherwise noted on a Bruker Avance 300 and Avance 400 spectrometer. FT-IR spectra were recorded on a Bruker EQUINOX55 spectrophotometer. UV–Vis absorption spectra were recorded on a Shimadzu 3100S spectrophotometer. Steady-state fluorescence spectra were recorded on a Perkin–Elmer LS-50. TGA and DSC analyses were carried out under nitrogen flow at a heating rate of 10 and 5 °C/min on a DuPont2200 instrument. Cyclic voltammometry was carried out on a Autolab PGSTAT12 potentiostat/galvanostat voltametric analyzer. Electrolysis was carried out using a

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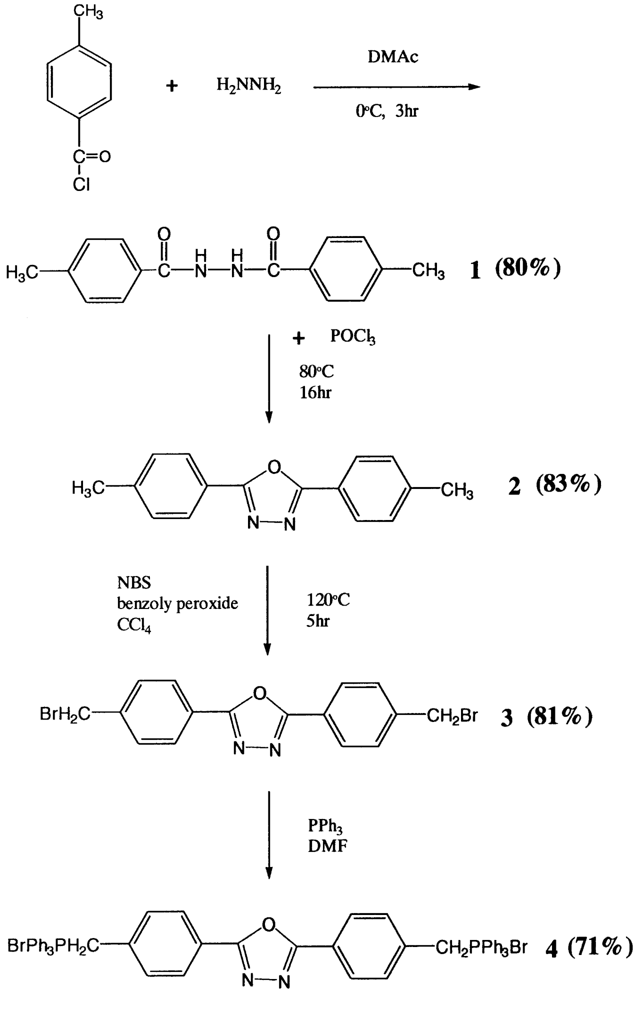
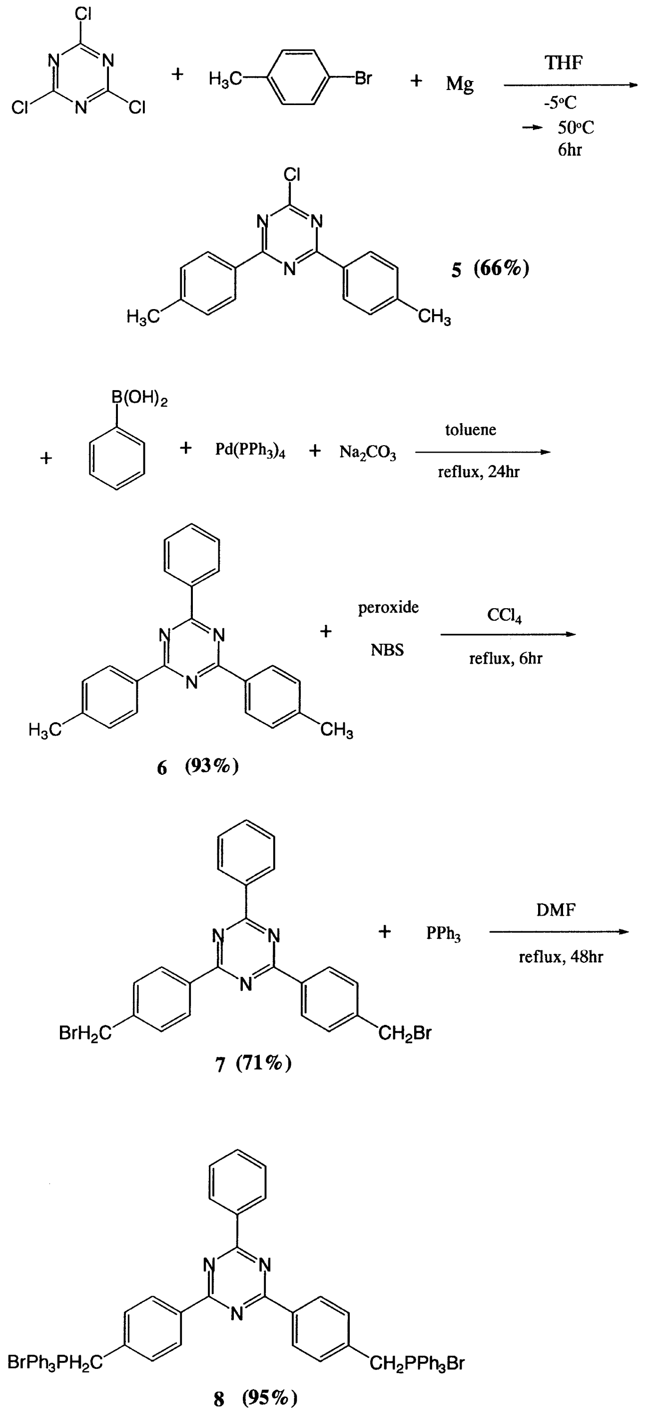


Scheme 1. Synthesis of monomer **4**.



Scheme 2. Synthesis of monomer **8**.

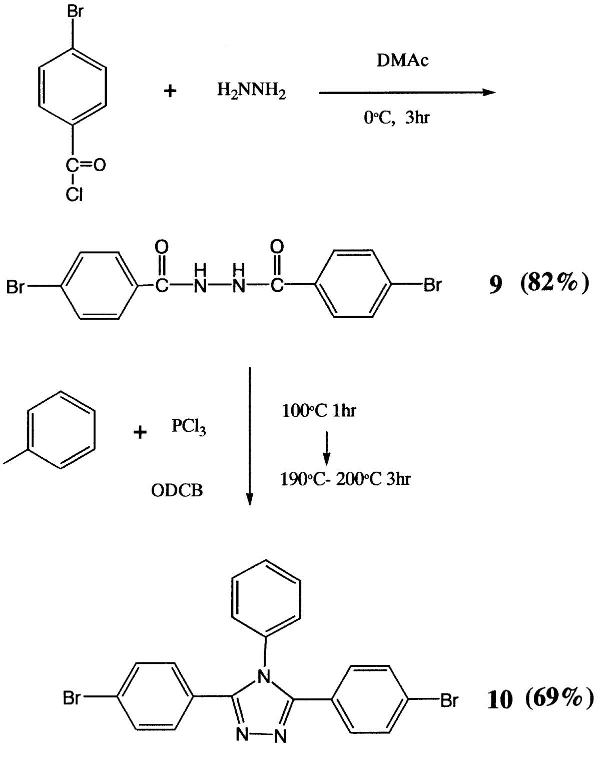
three-electrode cell in acetonitrile containing 0.1 M tetrabutylammonium tetrafluoroborate ($Bu_4N\ BF_4$) as the electrolyte. A platinum wire functioned as counter electrode, while the reference electrode was a 0.1 M $Ag/AgNO_3$ electrode. The working electrode was the polymer-coated platinum wire. The EL spectra were recorded using Minolta CS-1000. The current/voltage and luminescence/voltage characteristics were measured by current/voltage source (Keithly 238) and Minolta LS-100.

2.2. Synthesis of monomers

The synthetic routes of monomers are shown in Schemes 1–4.

2.2.1. Bis(4-methylphenyl)hydrazine (1)

p-Toluoyl chloride (48.7 g, 315 mmol) in dried *N,N*-dimethylacetamide (150 ml) was cooled to 0 °C and hydrazine (4.8 g, 150 mmol) was added. The reaction mixture was stirred for 4 h at 0 °C and then small amount of pyridine was added. Resulting solution was poured into ice water and precipitated. The precipitate was filtered and washed with cold methanol and then dried in the vacuum oven. The white solid product was obtained after recrystallization from methanol. The product yield was 32.0 g (80%). Mp: 257–258 °C. ^1H NMR (DMSO-d_6, ppm): δ 10.4(s, 2H), 7.8(d, 4H), 7.3(d, 4H), 2.3(s, 6H). ^{13}C NMR (DMSO-d_6, ppm): δ 165.7, 141.8, 129.8, 129.0, 127.4, 21.0.



Scheme 3. Synthesis of monomer **10**.

2.2.2. 2,5-Bis(4-methylphenyl)-1,3,4-oxadiazole (**2**)

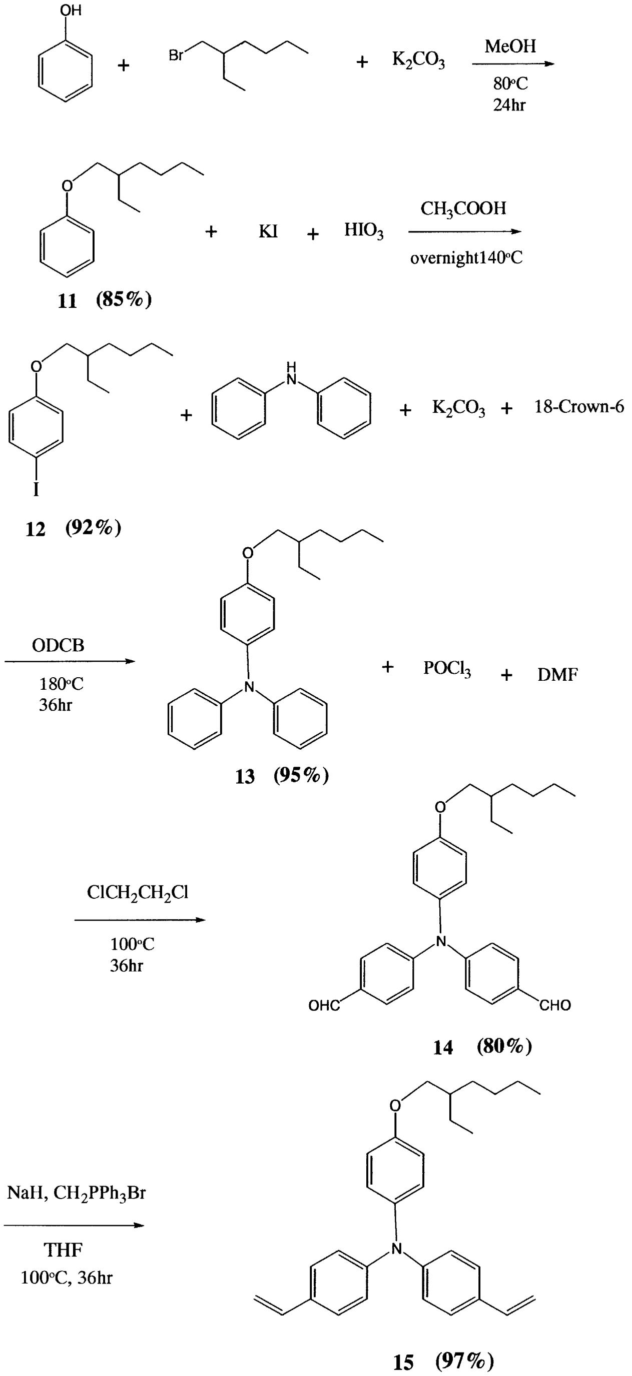
A mixture of bis(4-methylphenyl) hydrazine (10.7 g, 40 mmol) and $POCl_3$ (100 ml) as solvent was heated to 80 °C and stirred for 16 h at this temperature. After evaporating excess $POCl_3$, the residue was extracted with methylene chloride and washed with water. Crude product was recystallized from methanol and white solid (8.3 g) was obtained in 83% yield. Mp: 164–166 °C. ^{1}H NMR ($CDCl_3$, ppm): δ 8.0(d, 4H), 7.3(d, 4H), 2.4(s, 6H). ^{13}C NMR ($CDCl_3$, ppm): δ 164.4, 142.1, 129.7, 126.8, 121.2, 21.6.

2.2.3. 2,5-Bis[4-(bromomethyl)phenyl]-1,3,4-oxadiazole (**3**)

A mixture of 2,5-bis(4-methylphenyl)-1,3,4-oxadiazole (8.0 g, 32 mmol) and *N*-bromosuccinimide (12.5 g, 70 mmol) was dissolved in CCl_4 (150 ml) and catalytic amount of benzoyl peroxide was added. The reaction mixture was heated to 120 °C with stirring under Ar gas. After 5 h, resulting solution was filtered and extracted with methylene chloride and washed with water. The organic layer was evaporated under vacuum and crude product was recrystallized from methanol. White solid product was obtained in 81% yield (10.6 g). Mp: 224–225 °C. ^{1}H NMR ($CDCl_3$, ppm): δ 8.1(d, 4H), 7.5(d, 4H), 4.5(s, 4H). ^{13}C NMR ($CDCl_3$, ppm): δ 164.2, 141.6, 129.8, 127.4, 123.7, 32.2.

2.2.4. 2,5-Bis(4-tolylene-triphenylphosphonium bromide)-1,3,4-oxadiazole (**4**)

A mixture of 2,5-bis[4-(bromomethyl)phenyl]-1,3,4-oxadiazole (6.1 g, 15 mmol) and PPh_3 (8.6 g, 33 mmol) was dissolved in DMF (65 ml). The solution was stirred and refluxed for 24 h. The resulting solution was poured into diethyl ether. Filtered white solid was precipitated twice from diethyl ether: acetone = 3:1 solution. The product yield was 9.9 g (71%). Mp: 240–241 °C. ^{1}H NMR ($CDCl_3$, ppm): δ 7.8–7.5(m, 34H), 7.2(d, 4H), 6.1(d, 4H). ^{13}C NMR ($CDCl_3$, ppm): δ 163.6, 134.7, 134.4, 132.6, 131.8, 130.3, 130.1, 129.9, 122.6, 118.2, 117.3, 34.6. High



Scheme 4. Synthesis of monomers **14** and **15**.

resolution mass spectroscopy (HRMS): 928.1264 (calculated for $C_{52}H_{42}Br_2N_2OP_2$: 928.1234).

2.2.5. 2-Chloro-4,6-di-p-tolyl-1,3,5-triazine (**5**)

The cyanuric chloride (18.4 g, 100 mmol) was dissolved in tetrahydrofuran (THF) (100 ml) and cooled with ice–salt bath, then *p*-toluene magnesium bromide (46.9 g, 240 mmol) in THF (100 ml) was added slowly. After stirring at this temperature for 30 min, reaction mixture was warmed up slowly to 40–50 °C and maintained this temperature for 12 h. The resulting solution was quenched with NH_4Cl solution and THF was removed by evaporation. Dark yellow solution was extracted with methylene chloride and washed with water. Concentrated solution was poured into a large amount of methanol and filtered. Yellow solid was obtained in 66% yield (19.5 g). Mp: 204 °C. ^1H NMR ($CDCl_3$, ppm): δ 8.4(d, 4H), 7.3(d, 4H), 2.4(s, 6H). ^{13}C NMR ($CDCl_3$, ppm): δ 174.8, 171.9, 146.0, 130.0, 129.9, 21.9.

2.2.6. 2-Phenyl-4,6-di-p-tolyl-1,3,5-triazine (**6**)

A mixture of phenyl boronic acid (5.8 g, 48 mmol), $Pd(PPh_3)_4$(3 mmol) and 2-chloro-4,6-di-*p*-tolyl-1,3,5-triazine (11.8 g, 40 mmol) was dissolved with toluene (250 ml). This solution was added to 2 M Na_2CO_3 aqueous solution (50 ml) and refluxed for 24 h. After removing solvent, resulting solution was washed with water and extracted with methylene chloride. Crude product was recrystallized from methanol. The product yield was 12.6 g (93%). Mp: 204 °C. ^1H NMR ($CDCl_3$, ppm): δ 8.7(q, 2H), 8.6(d, 4H), 7.5(m, 3H), 7.3(d, 4H), 2.4(s, 6H). ^{13}C NMR ($CDCl_3$, ppm): δ 171.5, 171.4, 143.0, 136.5, 133.6, 132.3, 129.4, 129.0, 128.9, 128.6, 21.7.

2.2.7. 2,4-Bis(4-bromomethylphenyl)-6-phenyl-1,3,5-triazine (**7**)

This compound was prepared by the same method as used for 2,5-bis[4-(bromomethyl)phenyl]-1,3,4-oxadiazole. The product yield was 71%. Mp: 207 °C. ^1H NMR ($CDCl_3$, ppm): δ 8.7(m, 6H), 7.6(m, 7H), 4.6(s, 4H). ^{13}C NMR ($CDCl_3$, ppm): δ 171.1, 142.2, 136.2, 136.0, 132.6, 129.4, 129.3, 129.0, 128.7, 32.7.

2.2.8. 2,4-Bis(4-tolylene-triphenylphosphonium bromide)-6-phenyl-1,3,5-triazine (**8**)

This compound was prepared by the same method as used for 2,5-bis(4-tolylene-triphenylphosphonium bromide)-1,3,4-oxadiazole. The product yield was 95%. Mp: 228 °C. ^1H NMR ($CDCl_3$, ppm): δ 8.2(d, 2H), 8.0(d, 4H), 7.9(m, 12H), 7.7(m, 8H), 7.6(m, 14), 7.2(m, 3H), 5.9(d, 4H). ^{13}C NMR ($CDCl_3$, ppm): δ 170.8, 170.3, 135.0, 134.8, 134.6, 132.2, 132.1, 130.0, 129.9, 129.8, 128.5, 128.4, 128.1, 118.4, 117.6, 30.1. HRMS: 858.3168 (calculated for $C_{59}H_{46}N_3P_2$: 858.3167).

2.2.9. Bis(4-bromophenyl)hydrazine (**9**)

This compound was synthesized by the same method as used for bis(4-methylphenyl)hydrazine except starting from 4-bromobenzoyl chloride. The product yield was 82%. ^1H NMR (DMSO-d_6, ppm): δ 10.7(s, 2H), 7.8(d, 4H), 7.7(d, 4H). ^{13}C NMR (DMSO-d_6, ppm): δ 164.9, 131.6, 131.5, 129.5, 125.7.

2.2.10. 3,5-Bis-(4-bromophenyl)-4-phenyl-[1,2,4]triazole (**10**)

The aniline (11.2 g, 120 mmol) was dissolved in *o*-dichlorobenzene and PCl_3 (3.0 g, 22 mmol) was added. After heating to 100 °C for 1 h, the bis(4-bromophenyl) hydrazine (8.0 g, 20 mmol) was added to the reaction mixture. This solution was heated to 190–200 °C for 3 h and cooled to room temperature. The solution was digested in hot water and precipitated solid was collected by filtration. Crude solid was recrystallized from the mixture of small amount of glacial acetic acid and large amount of methanol twice. 69%, mp: 263 °C. ^1H NMR (DMSO-d_6, ppm): δ 7.6(d, 4H), 7.5(m, 3H), 7.4(m, 2H), 7.3(d, 4H). ^{13}C NMR (DMSO-d_6, ppm): δ 153.6, 134.3, 131.5, 130.4, 130.0, 129.9, 128.2, 126.1, 123.4. HRMS: 452.9531 (calculated for $C_{20}H_{13}Br_2N_3$: 452.9476).

2.2.11. 2-Ethylhexyloxy benzene (**11**)

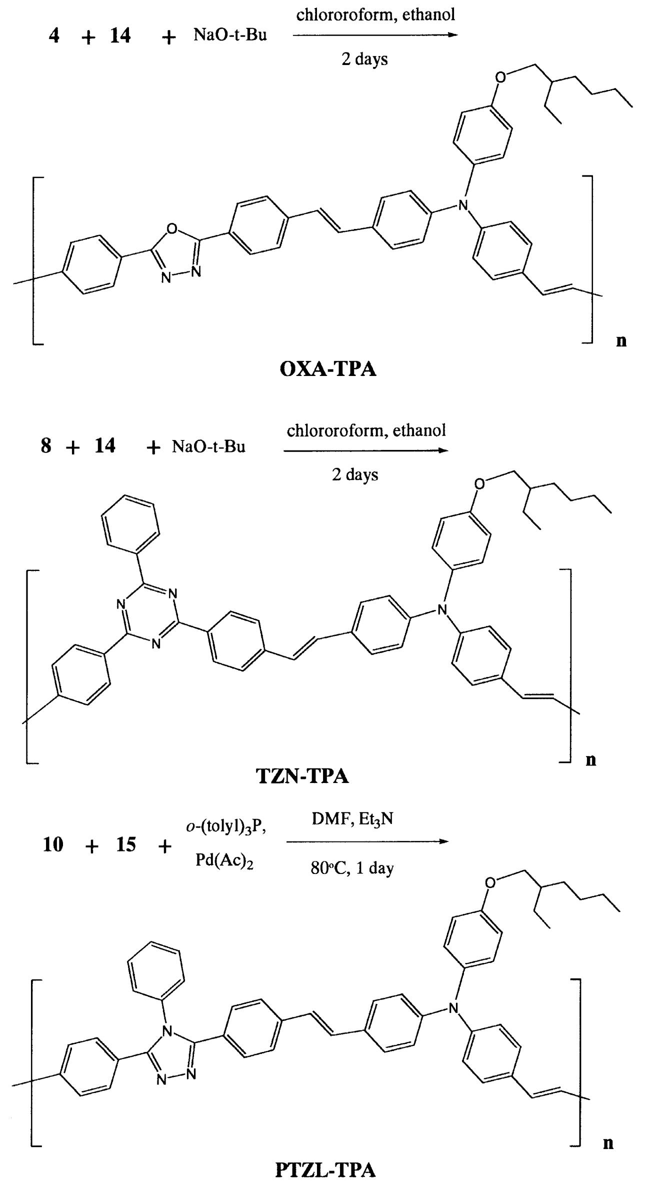
Phenol (23.5 g, 250 mmol), 2-ethylhexyl bromide (57.9 g, 300 mmol) and K_2CO_3 (43.2 g, 312 mmol) were added to methanol (240 ml) and refluxed for 24 h. After evaporating solvent, reaction mixture was worked up with ethyl acetate and water. Concentrated liquid was purified by column chromatography. Transparent liquid was obtained in 87% yield (45.0 g). ^1H NMR ($CDCl_3$, ppm): δ 7.3(m, 2H), 6.9(m, 3H), 3.8(d, 2H), 1.7(m, 1H), 1.3–1.4(m, 8H), 1.0(m, 6H). ^{13}C NMR ($CDCl_3$, ppm): δ 159.4, 129.3, 120.3, 114.5, 70.3, 39.4, 30.5, 29.0, 23.9, 23.0, 14.1, 11.1.

2.2.12. 2-Ethylhexyloxy-p-iodobenzene (**12**)

2-Ethylhexyloxy benzene (44.2 g, 214 mmol), potassium iodide (23.7 g, 143 mmol) and HIO_3 (12.5 g, 71 mmol) were dissolved in glacial acetic acid (220 ml) and refluxed overnight. After the solvent was evaporated from dark brown solution, remained iodine was quenched with sodium thiosulfate solution. Transparent solution was washed with water and extracted with diethyl ether. Crude liquid was purified by vacuum distillation. The product yield was 65.8 g (92%). ^1H NMR ($CDCl_3$, ppm): δ 7.5(d, 2H), 6.7(d, 2H), 3.8(d, 2H), 1.7(m, 1H), 1.3–1.5(m, 8H), 1.0(m, 6H). ^{13}C NMR ($CDCl_3$, ppm): δ 159.2, 138.0, 116.9, 82.3, 70.5, 39.2, 30.4, 29.0, 23.8, 23.0, 14.1, 11.1.

2.2.13. [4-(2-Ethylhexyloxy)-phenyl] diphenylamine (**13**)

2-Ethylhexyloxy-*p*-iodobenzene (30.7 g, 92 mmol), diphenylamine (10.4 g, 61.5 mmol), K_2CO_3 (34.0 g, 246 mmol), Cu (7.8 g, 123 mmol) and 18-crown-6 (1.6 g, 6.2 mmol) were dissolved in *o*-dichlorobenzene (120 ml) and refluxed until disappearance of the diphenylamine spot in the thin layer chromatography. Hot reaction mixture



Scheme 5. Preparation of the polymer and oligomers.

was filtered and solvent was removed by vacuum distillation. Crude product was purified by column chromatography and white solid (21.8 g) was obtained in 95% yield. ^{1}H NMR (CDCl$_3$, ppm): δ 7.2(m, 4H), 7.0(m, 6H), 6.9(m, 2H), 6.8(m, 2H), 3.8(d, 2H), 1.7(m, 1H), 1.3–1.5(m, 8H), 0.9(m, 6H). ^{13}C NMR (CDCl$_3$, ppm): δ 156.1, 148.2, 140.5, 129.0, 127.3, 122.8, 121.7, 115.3, 70.8, 39.5, 30.6, 29.1, 23.9, 23.0, 14.1, 11.1.

2.2.14. *[4-(2-Ethylhexyloxy)-phenyl]-bis-(4′-formylphenyl)amine (**14**)*

This compound was synthesized through well-known Vilsmeier–Haack formylation [17]. The product yield was 80%. ^{1}H NMR (CDCl$_3$, ppm): δ 9.8(s, 2H), 7.7(d, 4H), 7.1(d, 4H), 7.0(d, 2H), 6.9(d, 2H), 3.8(d, 2H), 1.7(m, 1H), 1.3–1.5(m, 8H), 0.9(m, 6H). ^{13}C NMR (CDCl$_3$, ppm): δ 190.3, 158.0, 152.1, 137.7, 131.2, 130.8, 128.8, 121.9, 116.0, 70.8, 39.4, 30.5, 29.0, 23.8, 22.9, 14.0, 11.1. HRMS: 429.2307 (calculated for $C_{28}H_{31}NO_3$: 429.2304).

2.2.15. *[4-(2-Ethylhexyloxy)-phenyl]-bis-(4′-vinylphenyl)amine (**15**)*

[4-(2-Ethylhexyloxy)-phenyl]-bis-(4′-formylphenyl)amine (6.4 g, 15 mmol) and methyltriphenyl-phosphonium bromide (12.9 g, 36 mmol) was dissolved in THF (120 ml) and then sodium hydride (1.8 g, 75 mmol) was added. The reaction mixture was refluxed for 36 h. After evaporating solvent, resulting solution was washed with water and extracted with methylene chloride. Crude product was purified by column chromatography. Bright yellow liquid was obtained in 97% yield (6.2 g). ^{1}H NMR (CDCl$_3$, ppm): δ 7.2(d, 4H), 7.0(d, 4H), 6.9(d, 2H), 6.8(d, 2H), 6.6(q, 2H), 5.6(d, 2H), 5.1(d, 2H), 3.8(d, 2H), 1.7(m, 1H), 1.3–1.5(m, 8H), 0.9(m, 6H). ^{13}C NMR (CDCl$_3$, ppm): δ 156.3, 147.6, 140.0, 136.2, 131.3, 127.4, 127.0, 122.6, 115.4, 111.8, 70.8, 39.5, 30.6, 29.1, 23.9, 23.0, 14.1, 11.1. HRMS: 425.2710 (calculated for $C_{30}H_{35}NO$: 425.2719).

2.3. *Preparation of a polymer and oligomers*

The polymerization methods are shown in Scheme 5.

2.3.1. *Preparation of PTZL–TPA*

The tri-*o*-tolylphosphine (0.07 g, 0.2 mmol), palladium acetate (0.01 g, 0.04 mmol), monomer **10**(0.5 g, 1 mmol) and **15**(10.46 g, 1 mmol) were dissolved into DMF and triethylamine (0.28 g, 2.5 mmol) was added to the mixture. The solution was stirred for 1 day at 80 °C. Cooled reaction mixture was poured into methanol and precipitated green solid was filtered and dried under vacuum. The polymer was purified by Soxhlet extraction of low molecular weight compounds for 4 days. Green solid (0.41 g) was obtained in 57% yield.

2.3.2. *Preparation of OXA–TPA and TZN–TPA*

A solution of sodium ethoxide (5 equiv.) in absolute ethanol was added to anhydrous chloroform/absolute ethanol solution of **14** (0.43 g, 1 mmol) and **4** (0.93 g, 1 mmol) (OXA–TPA) or **14** (0.86 g, 2 mmol) and **8** (2.04 g, 2 mmol) (TZN–TPA). The mixture was stirred for 24 h at room temperature. Resulting solution was washed with water and extracted with methylene chloride. Concentrated solution was dropped into methanol and polymer was precipitated. The polymer was filtered and dried under vacuum. Collected powder was purified again by Soxhlet extraction with methanol for 3–4 days. Product yield of OXA–TPA and TZN–TPA were 0.49 g (76%) and 1.2 g (81%), respectively.

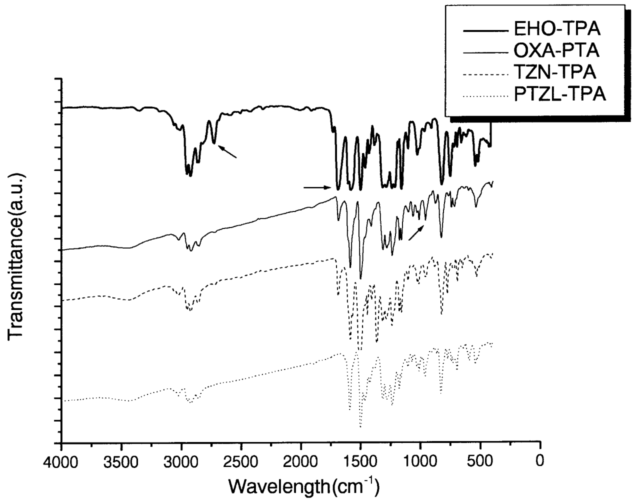


Fig. 1. The IR spectra of monomer **14**, OXA–TPA, TZN–TPA and PTZL–TPA. FT-IR spectra of polymers synthesized by Wittig reaction showed decrease of carbonyl stretching peak at 1694 cm^{-1} and alhehyde ν_{C-H} stretching peak at 2731 cm^{-1} **14** and a new peak at 961 cm^{-1} appeared in all the FT-IR spectra of polymer and oligomers.

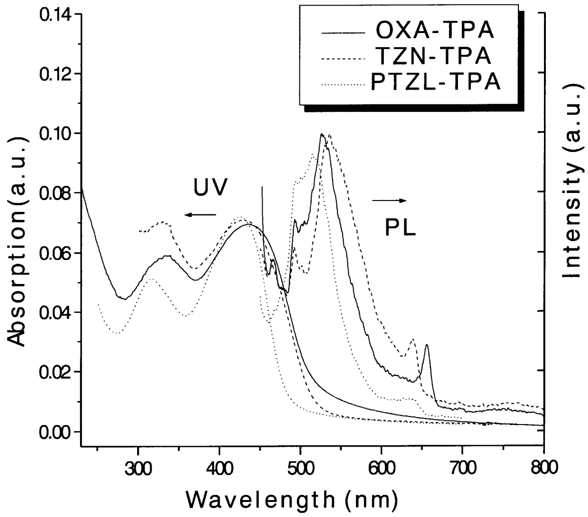


Fig. 2. UV absorption and PL spectra of the polymer and oligomers from thin films.

3. Results and discussion

The polymer PTZL–TPA was prepared by palladium catalyzed Heck reaction.

We intended to use the same Heck reaction for the synthesis of OXA–TPA and TZN–TPA, but the starting material, 2,5-bis(4-bromophenyl)-1,3,4-oxadiazole, could not be prepared from bis(4-bromophenyl)hydrazine and 1,4-dibromobenzene could not be used for Grignard reaction to prepare 2-chloro-4,6-di-*p*-bromobenzene-1,3,5-triazine because of dimerization or polymerization. We, therefore, utilized Wittig condensation reaction instead for the preparation of OXA–TPA and TZN–TPA.

The PTZL–TPA show a larger weight average molecular weight (M_w) (25,000) and a smaller polydispersity index (PDI) (1.2) than the other two polymers synthesized by Wittig condensation, OXA–TPA and TZN–TPA, which show a low M_w of 4000 and PDI of 1.8. The Wittig condensation reaction gave only the oligomers, not polymers. The molecular weight of all the materials prepared were determined by gel permeation chromatography with THF as eluent and polystyrene as the standard. The phosphonium bromide salts were destabilized by electron withdrawing 1,2,4-oxadiazole or 1,3,5-triazine group leading to the unbalanced stoichiometry of monomers and low molecular weight of polymers (oligomers) synthesized by Wittig condensation reaction can be attributed to this reason.

All the compounds synthesized were characterized by ^{1}H NMR, ^{13}C NMR, FT-IR and HRMS data. FT-IR spectra (Fig. 1) of OXA–TPA and TZN–TPA showed a sharp reduction of carbonyl stretching peak at 1694 cm^{-1} and alhehyde ν_{C-H} stretching peak at 2731 cm^{-1} in monomer **14**. New peak at 961 cm^{-1} corresponding to the out-of-plane bending mode of *trans*-vinylene groups appeared in all the FT-IR spectra of polymers indicating that *trans* double bond is generated by Wittig condensation reaction.

All the materials were soluble in common organic solvents such as chloroform, THF and 1,2-dichloroethane due to the presence of 2-ethylhexyl side chain attached on TPA moiety. Thin films of the polymers could be obtained with excellent reproducibility by spin-casting from 1,2-dichloroethane solution.

While electroluminescent organic polymers provide big advantages for device processing, a major drawback has been the low operating stability. When charge is applied to polymers, heat is generated and polymers are damaged by thermal degradation. Even though the two oligomers prepared had relatively low molecular weight, all the materials prepared exhibit remarkable thermal stability with high decomposition temperature and high glass transition temperature (T_g) as determined by TGA and DSC under nitrogen. The decomposition temperatures (T_d: 5% weight loss) of OXA–TPA, TZN–TPA and PTZL–TPA are 415, 421 and 329 °C, respectively. The DSC traces of the polymer and oligomers show high T_g; OXA–TPA: 123 °C, TZN–TPA: 114 °C, PTZL–TPA: 169 °C.

The UV–visible (Vis) absorption spectra of the three materials are similar to each other as shown in Fig. 2. The maximum absorption wavelength (λ_{max}) of the polymer and oligomers are shown at around 430 nm which is characteristic of conjugated polymer and absorption peaks near 330 nm are originated from TPA and electron-transporting units. The band gaps of OXA–TPA, TZN–TPA and PTZL–TPA, calculated from absorption band edges of 518, 517 and 483 nm, are 2.39, 2.40 and 2.57 eV, respectively.

The photoluminescence (PL) (Fig. 2) of OXA–TPA has a maximum peak at 525 nm, corresponding to green light emission. The EL (Fig. 3) spectrum showed a maximum peak at 535 nm. The PL and EL spectra of TZN–TPA showed a maximum emission peak at 535 and 560 nm,

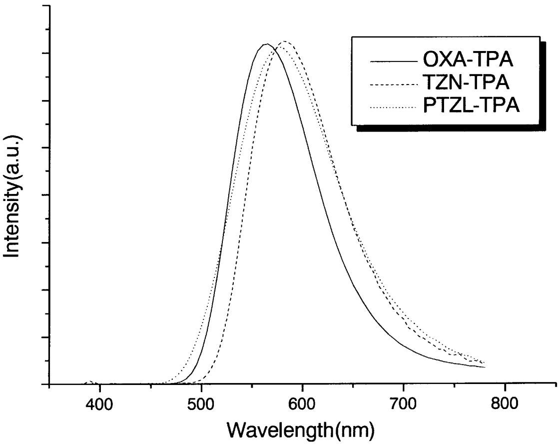


Fig. 3. EL spectra of the polymer and oligomers.

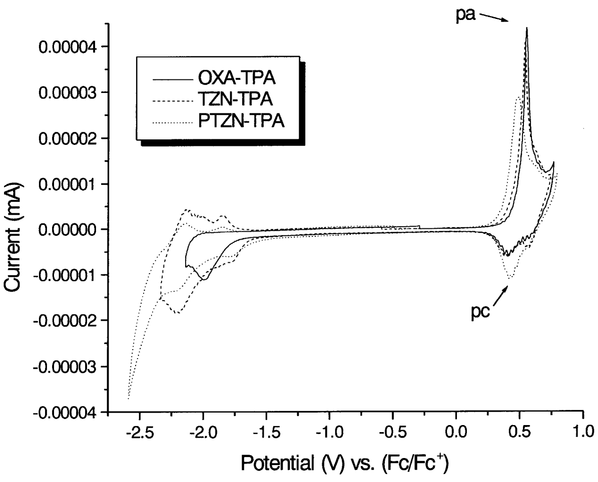


Fig. 4. CV data of the polymer and oligomers.

respectively, the region corresponding to green and yellowish-green light. The PL maximum peak of PTZL–TPA was 515 nm (blue-green), and EL maximum peak was 555 nm corresponding to yellowish-green light. The EL spectrum of PTZL–TPA was very broad covering a wide range and various colors. The broadening of EL spectrum of PTZL–TPA can be explained by CV data of the polymer. There are two inflection points in the reduction region in a CV curve of PTZL–TPA as shown in Fig. 4 indicating that PTZL–TPA has two different band gaps, in other words, PTZL–TPA have two different emission wavelengths and one of those is not shown in the PL. The first band gap is 2.51 eV (495 nm) that is similar to band gap calculated from UV band edge (2.57 eV = 483 nm) and the second one is shown at 2.19 eV (=567 nm). The first one corresponds to emission of PL and the second one is dominant in the emission of EL spectrum. Although the EL maximum peak seemed to correspond to the second band gap, the first band gap also has influence on the EL of PTZL–TPA and EL spectrum of PTZL–TPA is broadened.

The redox potential was recorded using CV to get information on the charge injection for the materials. All the CV data are obtained using a three-electrode cell in acetonitrile containing 0.1 M tetrabutylammonium tetrafluoroborate ($Bu_4N\ BF_4$) as the electrolyte. A platinum wire functioned as counter electrode, while the reference electrode was a 0.1 M $Ag/AgNO_3$ electrode. The working electrode was the polymer and oligomer-coated platinum wire. All the materials prepared possessed reversible oxidation peaks at relatively low potential. The energy levels of the polymer and oligomer were calculated using ferrocene (Fc) value of −4.8 eV as the standard ($E_{fc} = E_{Ag} - 0.089$ V). The HOMO (highest occupied molecular orbital) levels of materials were obtained as $E_{1/2}$ that were calculated as the average between E_{pa}(anodic peak) and E_{pc}(cathodic peak). The value of E_{pa} and E_{pc} corresponds to maximum and minimum peak of oxidation potential curve, respectively. The LUMO (lowest unoccupied molecular orbital) levels are estimated as deduction band gap calculated from UV edge from HOMO values. All the electronic parameters from CV are summarized in Table 1.

Introduction of the electron-transporting moiety (ETM) into the conjugated main chain is expected to give two effects. The one is to provide a site for electron injection because ETM is relatively electron deficient. Although the ETM is conjugated with the polymer backbone, the local electron density at ETM is still less than those of other units (phenylenevinylene and TPA). The other effect of ETM on the main chain is to lower the energy level of LUMO of the polymers facilitating electron injection and transport. Introducing ETM into the side chain of a polymer would only

Table 1
Electrochemical potentials and energy levels of the polymer and oligomers

	UV_{Edge} (nm)	Oxidation				HOMO[a] (eV)	LUMO[b] (eV)
		E_g (V)[c]	E_{pa} (V)	E_{pc} (V)	$E_{1/2}$ (V)		
OXA–TPA	518	2.39	−0.55	−0.41	−0.48	−5.28	−2.89
TZN–TPA	517	2.40	−0.54	−0.40	−0.47	−5.27	−2.87
PTZL–TPA	483	2.57	−0.49	−0.41	−0.45	−5.25	−2.68

[a] HOMO levels were converted from measured oxidation potentials assuming the absolute energy level of Fc to be −4.8 eV [18].

[b] LUMO levels were estimated from the HOMO levels and energy gaps.

[c] Band gaps were calculated from the absorption spectra of the polymer films.

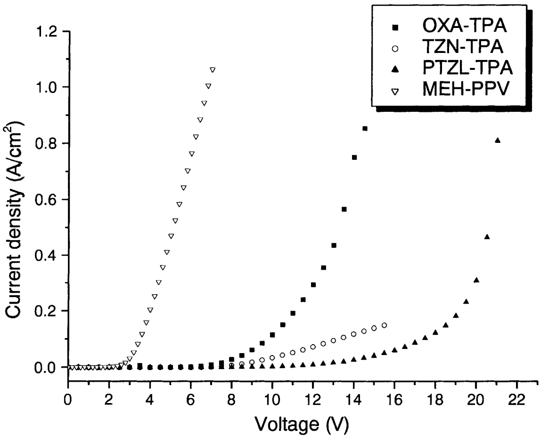


Fig. 5. *I–V* (current vs. voltage) curve of the polymer, oligomers and MEH–PPV.

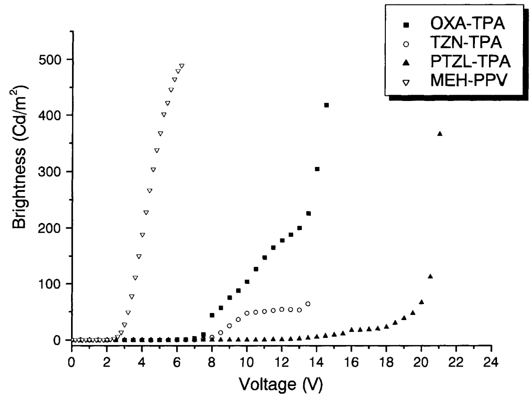


Fig. 6. *L–V* (luminescence vs. voltage) curve of the polymer, oligomers and MEH–PPV.

provide the first effect. However, the electrochemical results were in opposite to expectation. The HOMO levels (∼−5.3 eV) and LUMO levels(−2.7 to −2.9 eV) are similar to those of other PPV derivatives. All the materials (OXA–TPA, TZN–TPA and PTZL–TPA) have three parts—electron-transporting unit as ETM, hole-transporting unit (TPA) and light-emitting unit (phenylenevinylene). Initially, the contribution of emitting unit for charge injection and transporting was not considered, but emitting unit, phenylenevinylene, acted as hole-transporting unit like PPV. This resulted in unexpected imbalance of charge transporting. It is expected that the introduction of the both electron and hole-transporting moiety into the conjugated main chain will improve the EL efficiency by the balance of charge mobility. However, electron mobility was still less dominant in the EL layer.

The devices consisting of ITO/polymer and oligomers (90 nm)/LiF(1 nm)/Al(100 nm) configurations were fabricated under atmospheric condition to measure the electroluminescent properties of the polymers. In spite of low molecular weight of two oligomers, thin and uniform films were prepared by spin-coating of oligomer solution. The *I–V–L* curves of polymers and MEH–PPV are shown in Figs. 5 and 6. The device of MEH–PPV is used as reference to compare with prepared polymers and is fabricated as the same size and shape of the sample polymer devices. The MEH–PPV showed lower turn on voltage because HOMO level of MEH–PPV (−4.98 eV) is nearer to ITO (−4.8 eV) [19]. However, the brightness of MEH–PPV is similar to that of OXA–TPA and PTZN–TPA and the results are comparable with the performance of the other single layer devices of PPV derivatives [20]. The near linear relationship of light vs current for all the polymer and oligomers indicates that the light is produced by the combination of injected charges from both electrodes. The *I–V* and *L–V* curves of materials showed similar tendency that OXA–TPA has the lowest turn-on voltage and PTZL–TPA has the lowest electroluminescent properties indicating that 1,3,4-oxadiazole unit improved the electron injection and transporting property the best. The 1,2,4-triazole has been widely used as hole-blocking/electron-transporting material (HBETM) in the multilayer devices. We expected efficient EL performance for PTZL–TPA single layer EL devices and fabricated only single layer devices. However, hole-blocking property is less useful in single layer devices than electron-transporting property. The 1,3,4-oxadiazole has been well-known and most widely used electron-transporting material and this ET unit improves the single layer device performance very much and OXA–TPA has better EL property and lower turn-on voltage. PTZL–TPA can contain more impurities because of more complex preparation procedures and larger molecular weight giving the lowest device performance of PTZL–TPA.

4. Conclusions

A novel polymer and oligomers possessing both hole and electron-transporting units in the main chain were synthesized by palladium catalyzed Heck reaction (PTZL–TPA) and Wittig condensation reaction (OXA–TPA, TZN–TPA). The polymer generated by palladium catalyzed Heck reaction shows a large M_w (25,000) and small PDI (1.2) but materials synthesized by Wittig condensation show a M_w of 4000 and a PDI of 1.8. All the compounds were characterized by ^{1}H NMR, ^{13}C NMR, HRMS and FT-IR spectra. The two oligomers showed good film property when fabricated by spin-coating despite of the low molecular weight. All the materials prepared exhibit remarkable thermal stability with high decomposition temperature and high T_g as determined by TGA and DSC under nitrogen atmosphere. The EL emission maximum peaks of polymer and oligomers were 535–560 nm corresponding to green–yellowish-green. Among the three ETM, the 1,3,4-oxadiazole unit improved the electron injection and transporting property the best.

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