Synthesis and characterization of poly(terphenylenevinylene) derivative with electron withdrawing CN group and an electron donating alkoxy group

Yun-Hi Kim, Dong-Cheol Shin, Soon-Ki Kwon*

Department of Polymer Science & Engineering and Engineering Research Institute, Gyeongsang National University, Chinju 660-701, South Korea

Abstract

New poly(terphenylenevinylene) derivative with an alkoxy group and an electron withdrawing cyano group, poly(1,4-phenylene-2′-methoxy-5′-ethylhexyl-1′,4′-phenylene-1″,4″-phenylene-α-cyanovinylene), was synthesized via the Suzuki coupling reaction. The polymer was completely soluble in common organic solvent and showed good thermal stability up to 380 °C. The presence of the electron withdrawing cyano group lowered LUMO energy level and the presence of the electron donating alkoxy group increased HOMO energy level of the polymer relative to those of poly(terphenylenevinylene). Light emitting diodes (LEDs) with the configuration ITO/PTPCNV/Al and ITO/PPV/PTPCNV/Al were fabricated. ITO/PTPCNV/Al device showed turn on voltage of 5 V (0.005 mA), however, ITO/PPV/PTPCNV/Al exhibited turn on voltage of 2.5 V (0.003 mA). The maximum brightness of the ITO/PPV/PTPCNV/Al device is about 5200 cd/m^2 at 8 V with a maximum efficiency of 1.243 lm/W. The EL spectrum of the ITO/PPV/PTPCNV/Al device, which was consistent with PL spectrum of PTPCNV, had a maximum peak at 491 nm with a shoulder peak at around 520 nm.

1. Introduction

Since the first report of polymer light-emitting diodes based on poly(*p*-phenylenevinylene) (PPV) by the Cambridge group [1], a great number of efforts have been devoted to the synthesis of light emitting polymers because of several advantages over small organic molecules, excellent mechanical properties and simple fabrication method of spin casting, etc [2,3]. Many conjugated polymers include PPV, poly(2-methoxy-5,2′-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV) [4], poly(*p*-phenylene) derivatives (PPPs) [5], polyfluorene derivatives (PFs) [6], and polythiophene derivatives (PThs) [7] have been synthesized for as emissive and/or charge transporting materials in polymer light emitting diodes (PLED). However some important issues such as balancing of charge injection, device stability, and color tunability remain to be addressed.

To improve the device efficiency of PLEDs, it is necessary to balance the rate of injection of electrons and holes from opposite electrodes into the device [8]. Many approaches have been taken to overcome the imbalance of charge carrier injection or mobility. The most common practices have been either to use a charge carrier transporting material to block the major charge carrier and to enhance the injection of the minor charge carrier or to align the energy band of the polymer by introducing electron withdrawing groups as pendant groups or as part of the polymer backbone. Bredas et al. have shown that introduction of an electron withdrawing group onto the arylene ring or the vinyl group of PPV lowers the HOMO and LUMO energies of the polymer, thereby permitting the use of a higher work function metal in the LED device. For the most of conjugated polymers including PPV derivatives, the barrier of electron injection is much higher than that of hole injection. Therefore, many substituents including CN [9–13], oxadiazole [14–19], triazole [14,15], pyridine [16],

quinoxaline [17], thiadiazole [18–22], etc. which have a high electron affinity have been introduced [23].

Recently, we reported the synthesis and characterization of poly(terphenylenevinylene) derivatives and poly(biphenylenevinylene) derivatives with a controlled conjugation length of terphenylene vinylene unit and biphenylene vinylene unit [24–27]. They showed good blue electroluminescent characteristics. Efficient thermally stable blue light emitting materials are needed both to complete the color spectrum and serve as energy transfer media for incorporated fluorophores [28–32].

Thus, in the present article, we tried to synthesize poly(terphenylenevinylene) derivative containing electron withdrawing CN group in the vinyl bridge and electron donating alkoxy group in the main chain. It is expected that the polymer will have high efficiency due to the balanced charge carriers.

2. Experiment

2.1. 2-Methoxy-[5-(2′-ethylhexyl)oxy]-1,4-benzene diboronic acid (MEHBBA)

2-Methoxy[5-(2′-ethylhexyl)oxy]-1,4-dibromobenzene (40 g, 0.104 mol) was added dropwise to magnesium powders (7.4 g, 0.304 mol) in boiling THF (250 ml). The reaction mixture was refluxed for 2 h and cooled to −70 °C using liquid nitrogen. After the addition of undiluted trimethyl borate (42 g, 0.404 mol), the reaction mixture was stirred for 12 h at room temperature. Then 300 ml of 2 M H_2SO_4 solution was added. The organic layer was extracted, washed with water, dried over $MgSO_4$ and filtered. The solvent was evaporated off. The residue was recrystallized from ethyl acetate to give white crystals. Yield=20%, mp=200 °C, ^{1}H NMR (CDCl₃, ppm): δ 7.1 (s, 1H), 7.0 (s, 1H), 6.2 (s, 4H), 3.6 (d, 2H), 3.5 (s, 3H), 1.3 (m, 1H), 1.2–1.0 (m, 8H), 0.6–0.5 (m, 6H), ^{13}C NMR (acetone-*d*, ppm): 206.4, 205.9, 159.5, 159.2, 119.3, 118.3, 71.7, 56.3, 40.4, 31.4, 30.5, 24.8, 23.6, 14.3, 11.4. FT-IR (KBr) (cm^{-1}): 3355, 2928, 2871, 1497, 1387, 1308, 1245, 1202, 1136, 1099, 1059, 885, 777, 718, 645, 554. Cacld for $C_{15}H_{26}B_2O_6$: C, 55.61, H, 8.09. Found: C, 55.61, H, 8.11.

2.2. 1,2-Bis(4-bromophenyl)-1-cyanoethene (BPCNE)

4-Bromophenylacetonitrile (1.06 g, 5.4 mmol) and 4-bromobenzaldehyde (1.00 g, 5.4 mmol) were dissolved in 50 ml of dry ethanol under nitrogen atmosphere in 100 ml 2-neck round flask. The mixture of sodium hydroxide (0.25 g, 6.25 mmol) and 10 ml of dry ethanol was added slowly, and then the crude product was precipitated in the reaction mixture. The reaction mixture was stirred for 1 h at room temperature, and the precipitate was filtered and washed with water. The powdery white product was obtained. Yield=95%, mp=122 °C, ^{1}H NMR (CDCl₃,

δ 7.8 (d, 2H), 7.7 (m, 4H), 7.6 (m, 2H), 7.5 (s, 1H), FT-IR (KBr) (cm^{-1}): 3080, 2250, 1550, 1499, 1430, 760. Anal. Cacld for $C_{15}H_9Br_2N$: C, 49.62; H, 2.50; N, 3.86. Found: C, 49.60; H, 2.53; N, 3.84.

2.3. Poly(1,4-phenylene-2′-methoxy-5′ethylhexyl-1′,4′-phenylene-1″,4″-phenylene-α-cyanovinylene) (PTPCNV)

All handling of catalysts and polymerization was done in a nitrogen atmosphere. To a stirred solution of 1-methoxy[4-(2′-ethylhexyl)oxy]benzene diboronic acid (0.578 g, 1.786 mmol), 2,3-bis(4′-bromophenyl)-acrylonitrile (0.648 g, 1.786 mmol) in 10 ml THF and 4 ml 2 M K_2CO_3 solution in water was added catalysts, $Pd(PPh_3)_4$ (8.4 mg, 0.6 mol%). The reaction mixture was heated at 80 °C under nitrogen atmosphere for 8 h. Bromobenzene (0.05 g, 0.318 mmol) was added and then phenyl boronic acid (0.05 g, 0.41 mmol) was added with small amounts of catalysts for end-capping. After 2 h, the reaction mixture was poured into methanol (50 ml) and filtered with glass filter. The residue was dissolved in CHCl₃ and washed with waters. After being dried over $MgSO_4$, precipitation was twice repeated with chloroform/methanol. Yield: 0.6 g (60%). ^{1}H NMR (CDCl₃, ppm): δ 6.9–7.8 (m, 11H, aromatic and vinylic), 3.7–3.8 (m, 5H, OCH₂ and CH₃), 1.9–0.8 (m, 15H). ^{13}C NMR (CDCl₃, ppm) δ 140.5, 138.3, 131.6, 131.3, 130.6, 129.2, 129.0, 128.2, 128.0, 126.5, 125.9, 124.8, 124.5, 121.5, 117.2, 114.8, 113.5, 70.9, 55.5, 38.7, 30.6, 28.7, 23.1, 14.3, 13.1, 10.1. FT-IR (KBr) (cm^{-1}): 3100, 3000, 2950, 2925, 2872, 2250, 1495, 1385, 1245, 1093, 1057, 776, 716. Anal. Cacld for $C_{30}H_{31}NO_2$: C, 82.35; H, 7.14; N, 3.20. Found: C, 82.34; H, 7.11; N, 3.22.

2.4. Fabrication of LED

PPV as hole injection (transporting) layer (100 Å) was coated by conventional methods onto iridium tin oxide coated glass substrate, which was washed with water, aceton, and isopropyl alcohol, sequentially. After spin coating of PPV, the film was thermally heated for 2 h under nitrogen atmosphere. A thin PTPCNV film (1700 Å) was spin coated (3000 rpm, 50 s) from a 2.0 wt% solution of the polymer onto PPV. Aluminum electrode (1300 Å) was deposited on top of the polymer film at high vacuum (below 1×10^{-5} Torr.). Wires were attached to both electrodes with a conductive epoxy adhesive.

3. Results and discussion

The synthetic route for poly(terphenylene-α-cyanovinylene) containing alkoxy and CN groups is described in Scheme 1. 2-Methoxy-[5-(2′-ethylhexyl)oxy]-1,4-benzene diboronic acid and 1,2-bis(4-bromophenyl)-1-cyanoethene as the monomers were obtained by Grignard and Knoevenagel reactions, respectively. The monomers of high purity
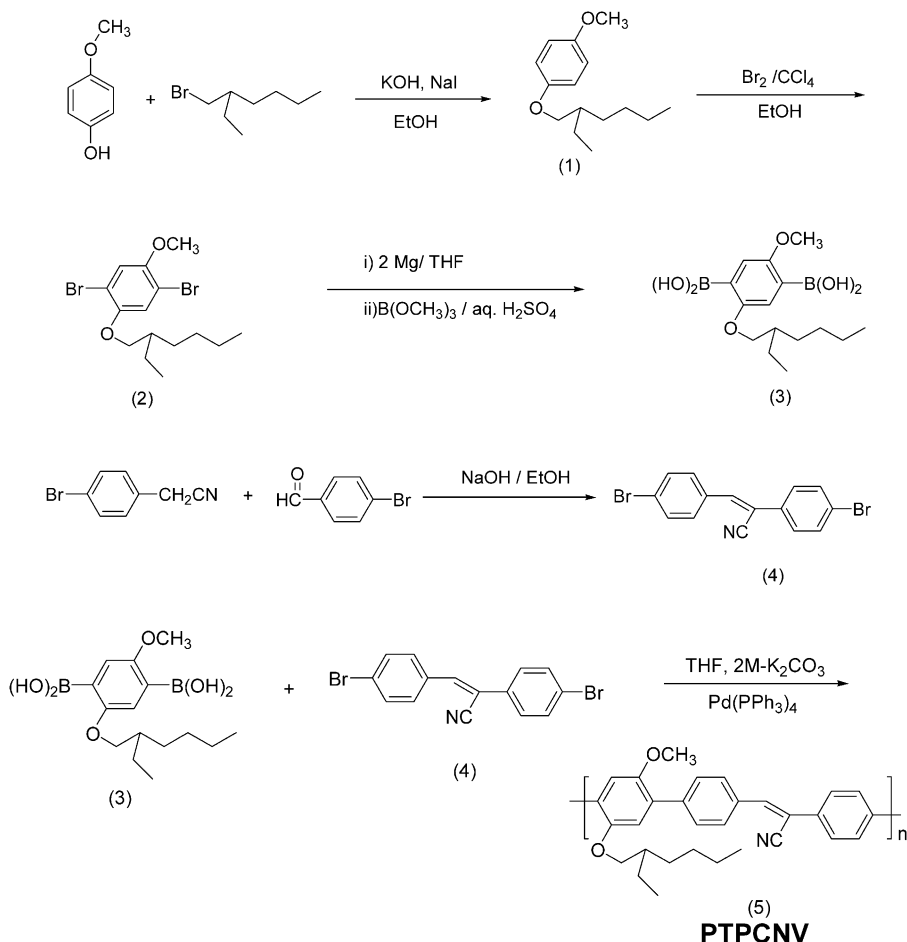
Scheme 1.

were obtained by successive crystallization. The products of each step were characterized by spectroscopic methods such as ^{1}H NMR and FT-IR. Cyano modified polymer 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. This method has some drawbacks because side reactions may take place, which precludes the production of defect free structures. Poly (terphenylene-α-cyanovinylene) derivative (PTPCNV) was synthesized through the Suzuki reaction of diboronic acid and dibromide, and following end capping reaction. The chemical structure of obtained polymer was confirmed by ^{1}H and ^{13}C NMR, FT-IR and elemental analysis. In the FT-IR spectrum, the disappearance of characteristics absorption bands of diboronic acid (3355 cm^{-1}) confirmed the completion of polymerization. In the ^{1}H NMR spectrum, the vinyl protons appeared at around 6.85 ppm with aromatic protons. Methoxy and oxymethylene proton peaks showed at around 3.8 ppm. All other peaks showed good correspondence with the chemical structure of polymer. (Fig. 1) The obtained polymer was soluble in chloroform, hot chlorobenzene, and toluene, partly soluble

in THF, benzene, toluene, methylenechloride, and insoluble in the highly polar and nonpolar solvents such as DMF, DMSO, methanol, and acetone etc. The molecular weight of PTPCNV was determined by gel permeation chromatoraphy using polystyrene standards. The weight average molecular weight (M_w) of the PTPCNV was about 10,000 (PDI = 1.43).

The thermal stability of the polymer was evaluated by thermogravimetric analysis (TGA) under a nitrogen atmosphere at a heating rate of 10 °C/min. Fig. 2 shows that the polymer exhibits good thermal stability. The polymer has onset degradation temperature above 320 °C, and 5% weight loss was observed at above 380 °C.

The UV–vis absorption and photoluminescence spectra of PTPCNV in chloroform are shown in Fig. 3. The maximum absorption and band gap of the polymer estimated from the absorption spectrum edge are 380 nm and 2.8 eV, respectively. Upon UV excitation at 380 nm, the photoluminescence of the polymer has maximum emission at 480 nm corresponding greenish blue light. In the UV-absorption of the PTPCNV film, the maximum is observed at 410 nm. It is known that CN-PPV has maximum absorption at around 550 nm [8]. This considerable blue
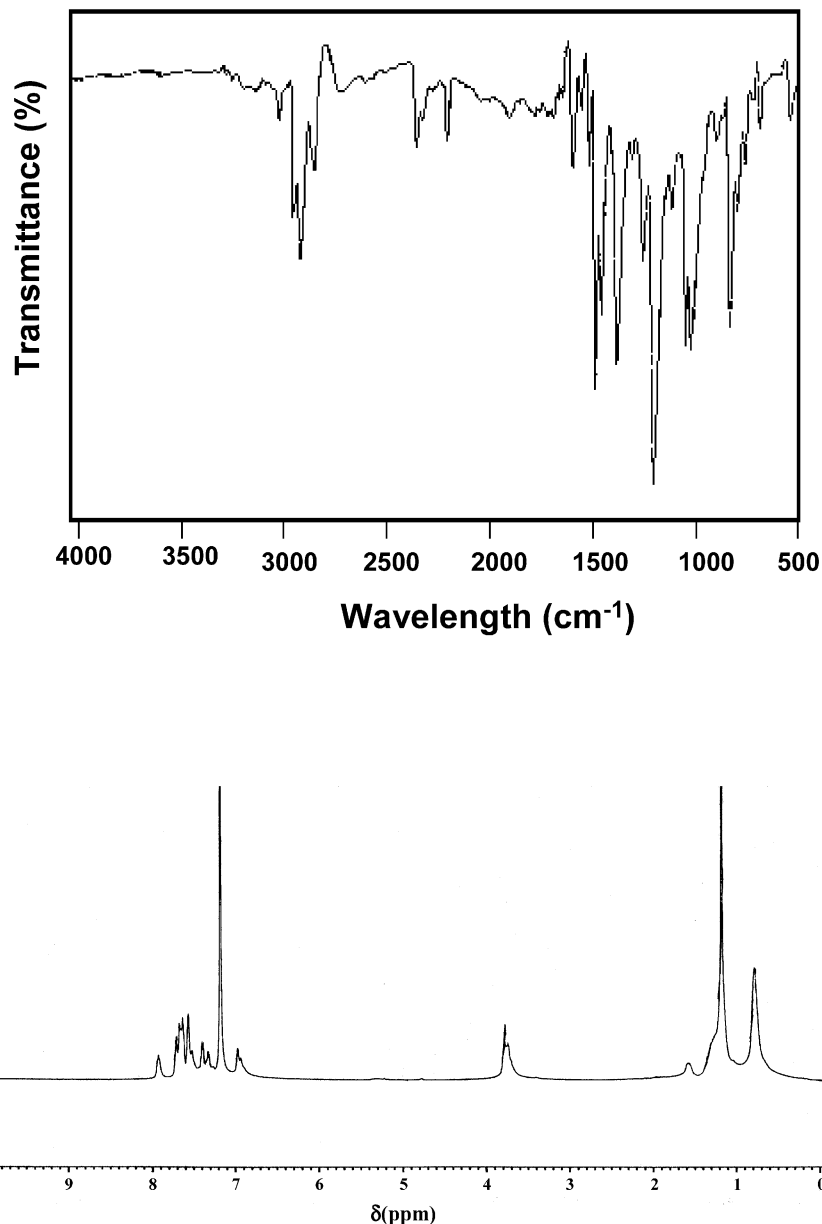
Fig. 1. FT-IR and ^{1}H NMR spectrum of PTPCNV.

shift was believed to be resulted from terphenylenevinylene backbone. Upon UV excitation at 410 nm, the photoluminescence spectrum of the PTPCNV had a maximum peak at 491 nm with a shoulder peak at around 520 nm. The red shift from that of the solution can be attributed either to the difference in the energy transfer processes between the film and the solution due to the presence of rotational conformers in the solution reducing the π conjugation of the chromophore, or to the effect of packing and local geometry of the polymers [33].

Cyclic voltammetry (CV) was employed to estimate its HOMO and LUMO energy level. The electrochemical process probed by cyclic voltammetry is similar to it involved in the charge injection and transport process in LED devices. The polymer film was coated onto a Pt electrode and scanned positively and negatively at a scan rate of 100 mV s^{-1} in a 0.1 M solution of Bu$_4$NClO$_4$ in anhydrous acetonitrile. The onset potential for reduction and oxidation was observed at about -1.78 and 0.97 V, respectively. From the onset potential of the oxidation and reduction processes, the band gap of the polymer was estimated to be 2.75 eV, which is consistent with the result of absorption edge. According to the equations, the LUMO and HOMO of polymer was estimated to be -3.02 and -5.77 eV, respectively [34,35]. The electrochemical data from cyclic voltammetry indicate that the introduction of cyano electron withdrawing functionality leads to a significant increase in electron affinity (E_a) from the -2.85 eV for poly(terphenylenevinylene) to -3.02 eV for PTPCNV [26,27]. This demonstrates the effectiveness
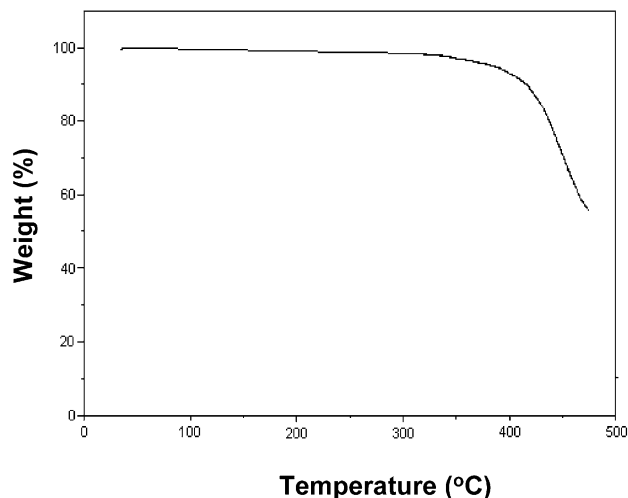
Fig. 2. TGA thermogram of PTPCNV.

of cyano group in improving charge injection property of polymer. And the introduction of electron donating alkoxy group in the main also leads slightly increase in oxidation ability from 5.83 eV for poly(terphenylenevinylene) to 5.77 eV for the obtained PTPCNV.

Electroluminescent devices were constructed with the structure ITO/PTPCNV/Al and ITO/PPV/PTPCNV/Al. The PPV as buffer layer was prepared by the sulfonium precursor route, which can be deposited as a high quality thin film [36]. This has the advantage that, after thermal conversion, the resulting polymer is not soluble in the solvent used to deposite. Fig. 4 shows the characteristics of the current and emission-light intensity against voltage on the devices. For ITO/PTPCNV/Al device, turn on voltage showed at 5 V (0.005 mA), and current increases much more rapidly than the emitted light intensity does as the voltage increases. This may be due an unbalanced injection of the carries. However, LED with PPV layer exhibited turn
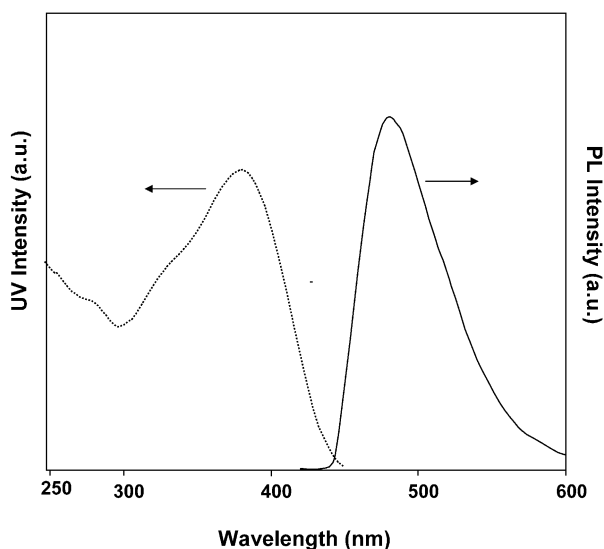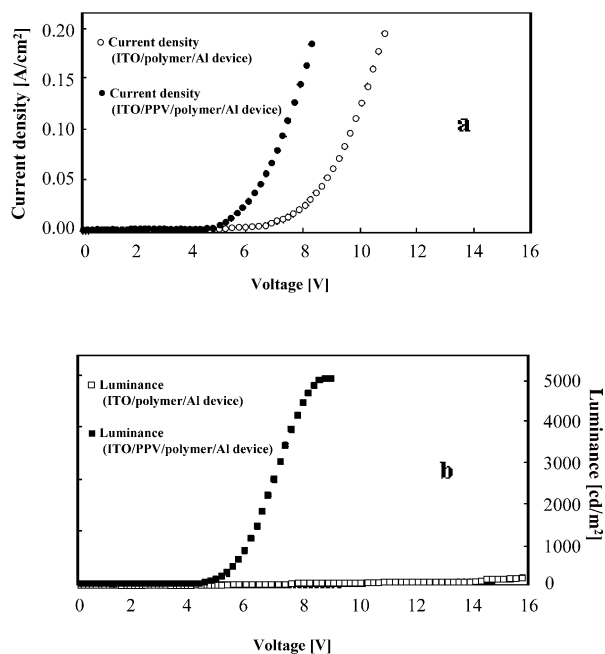

Fig. 4. The characteristics of the current vs voltage and emission-light intensity vs voltage of the ITO/PTPCNV/Al device and ITO/PPV/PTPCN-V/Al device.

on voltage of 2.5 V (0.003 mA) and not only the turn on voltage for current is the same as that for light emission but also the dependence of light-emission on the voltage closely follows the current–voltage curve. The reduced turn-on voltage is due to the higher work function of PPV compared to that of PTPCNV and improved contact between ITO/PTPCNV interface. And it also indicates an equally efficient injection and transport of the both carries. The maximum brightness of the ITO/PPV/PTPCNV/Al device is about 5200 cd/m^2 at 8 V with a current density of about 0.18 A/cm^2. The maximum efficiency of the ITO/PPV/PTPCNV/Al device is 1.24 lm/W at 133 cd/m^2 and 5 V.

Fig. 5 shows the electroluminescence spectra of ITO/PPV/PTPCNV/Al device and ITO/PPV/Al device, and solid

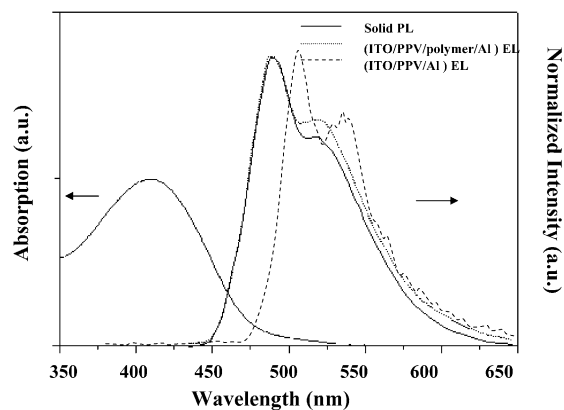Fig. 3. UV–vis absorption and PL spectra of PTPCNV in CHCl$_3$.

Fig. 5. Solid PL spectrum of PTPCNV and EL spectra of ITO/PPV/PTPCN-V/Al device and ITO/PPV/Al device.

photoluminescence spectrum of PTPCNV. The EL spectrum of the ITO/PPV/PTPCNV/Al device had a maximum peak at 491 nm with a shoulder peak at around 520 nm corresponding to bluish green light. The EL spectrum is consistent with solid PL spectrum of PTPCNV. Identity of the PL and EL spectrum suggests that holes and electrons recombinate in the PTPCNV as emitting layer. Fig. 6 shows the hypothesized energy level diagram of ITO/PPV/ PTPCNV/Al device fabricated in this work. From the results, the PPV film acts as an hole transporting and an electron blocking layer, and helps to shift exciton formation away from possible quenching centres near the metal electrodes as well as improved contact. And, the PTPCNV polymer with dual functions acts as an emitting as well as electron transporting material.

4. Conclusions

New poly(terphenylene vinylene) derivative with an electron withdrawing cyano group and electron donating alkoxy group, poly(1,4-phenylene-2'-methoxy-5'-ethyl-hexyl-1',4'-phenylene-1'',4''-phenylene-α-cyanovinylene), was synthesized via the Suzuki coupling reaction. The solution and solid photoluminescence maximum of the obtained polymer showed at 480 and 491 nm, respectively. The presence of the electron withdrawing cyano group and electron donating alkoxy group significantly lowered LUMO energy level and slightly increased HOMO energy level of polymer relative to those of poly(terphenylenevi-nylene), respectively. The ITO/PPV/PTPCNV/Al device exhibited turn on voltage of 2.5 V (0.003 mA) and the maximum brightness of 5200 cd/m^2 at 8 V. In the ITO/PPV/PTPCNV/Al device, the PTPCNV polymer with dual functions acts as an emitting as well as electron transporting material.
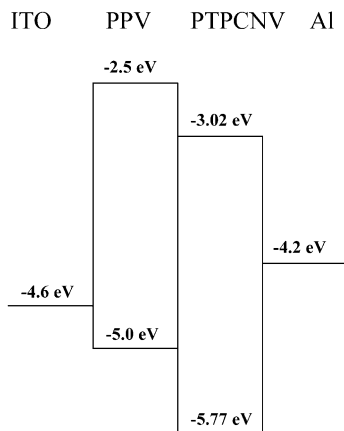
ITO   PPV   PTPCNV   Al

-2.5 eV

-3.02 eV

-4.2 eV

-4.6 eV

-5.0 eV

-5.77 eV

Fig. 6. The hypothesized energy level diagram of ITO/PPV/PTPCNV/Al device.

References

[1] Burroughes JH, Bradley DDC, Brown AR, Marks RN, Mackay K, Friend RH, et al. Nature 1990;347:539.
[2] Kraft A, Grimsdale AC, Holmes AB. Angew Chem, Int Ed 1998;37: 402.
[3] Friend RH, Gymer RW, Holmes AB, Burroughes JH, Marks RN, Taliani C, et al. Nature 1999;397:121.
[4] (a) Braun D, Heeger A. J Appl Phys Lett 1991;58:1982.
(b) Spreitzer H. Adv Mater 1998;10:1340.
[5] Birgerson J, Fahlman M, Broms P, Salaneck WR. Synth Met 1996;80: 125.
[6] (a) Fukuda K, Sawada K, Yoshino K. J Polym Sci, Polym Chem 1993;31.
(b) Ohmori M, Uchida M, Morishima C, Fujii A, Yoshino K. Jpn J Appl Phys 1993;32:1663.
(c) Ohmori Y, Uchida M, Muro K, Yoshino K. Jpn J Appl Phys 1991; 30:L1941.
[7] Berggren M, Gustafsson G, Inganas O, Andersson MR, Hjertberg T, Wennerstrom O. J Appl Phys 1994;76:7530.
[8] Greenham NC, Moratti SC, Bradley DDC, Friend RH, Holmes AB, Kraft A. Nature 1993;365:628.
[9] Moratti SC, Cervini R, Holmes AB, Baigent DR, Friend RH, Greenham NC, et al. Synth Met 1995;71:2117.
[10] Staring EGI, Demandt RCJE, Braun D, Rikken GLJ, Kessener YARR, Venhuizen AHJ, et al. Synth Met 1995;71:2179.
[11] Graham NC, Moratti SC, Bradley DDC, Friend RH, Holmes AB. Nature 1993;365:628.
[12] Brouwer HJ, Hiberer A, Krasnikov VV, Wertz M, Widerman J, Hadziioannou G. Synth Met 1997;84:881.
[13] Dottinger SE, Holoch M, Hohnholz D, Segura JL, Steihuber E, Hanack M. Synth Met 1997;84:267.
[14] Kwon SK, Kim YH, Shin SC. Bull Korean Chem Soc 2002;23:17.
[15] Strukelj MJ, Papadimitrakopoulos F, Miller TM, Rothberg LJ. Science 1995;267:2793.
[16] Strukelj MJ. J Am Chem Soc 1995;117:11976.
[17] Bettenhausen J, Strohrigel P. Adv Mater 1996;8:507.
[18] Shin DC, Ahn JH, Kim YH, Kwon SK. J Polym Sci, Polym Chem 2000;38:3086.
[19] Wu CC, Sturm JC, Register RA, Tian J, Dana EP, Thompson ME. IEEE Trans Electron Dev 1997;44:1269.
[20] Wang YZ, Gebler DD, Fu DK, Sweager TM, Macdiamid AG, Epstein AJ. Synth Met 1997;85:1179.
[21] Yamamoto T, Sugiyama KT, Lnone T, Kanbara T. J Am Chem Soc 1996;118:3939.
[22] Cui Y, Zhang X, Jenekhe SA. Macromolecules 1999;32:3824.
[23] Freudenmann R, Behnisch B, Lange F, Hanack M. Synth Met 2000; 111:441.
[24] Ahn BK, Kim YH, Shin DC, Park YS, Yu HS, Kwon SK. Macromolecules 2001;34:3993.
[25] Kim YH, Shin DC, Kwon SK, Lee JH. J Mater Chem 2002;12:1280.
[26] Kim YH, Ahn BK, Shin DC, Kim HS, Kwon SK. Opt Mater 2002;21: 175.
[27] Kim YH, Anh JH, Shin DC, Kim JH, Park YW, Choi DS, et al. Bull Korean Chem Soc 2001;22:1181.

[28] Chen C, Yang Y, Thompson ME, Kido J. Appl Phys Lett 2002;80: 2308.

[29] Fang-Iy ED, Sahadeva R, Ching FS, Michelle SL, Alex KY. J Chem Mater 2003;15:269.

[30] Becker S, Ego C, Grimsdal AC, List EJW, Marsitzky D, Pogantsh A, et al. Synth Met 2002;125:73.

[31] Mpallas JG, Spiliopoulos IK, Mikroyannidis JA. J Polym Sci, Polym Chem 2003;41:1091.

[32] Hongchao L, Yufeng H, Yanguang Z, Dongge M, Lixiang W, Xiabin J, et al. Chem Mater 2002;14:4484.

[33] Kim YH, Kwon K, You DS, Rubner MF, Wrighton M. Chem Mater 1997;9:2699.

[34] Kim YH, Shin DC, Kim SH, Ko CH, Yu HS, Chae YS, et al. Adv Mater 2001;13:1690.

[35] Janietz S, Bradley DDC, Grell M, Giebeler C, Inbasekaran M, Woo EP. Appl Phys Lett 1998;73:2453.

[36] Kim YH, Shin DC, Jung SO, Kwon SK. Mol Cryst Liq Cryst 2003; 405:27.