Synthesis, Properties, and Application of New Luminescent Polymers with Both Hole and Electron Injection Abilities for Light-Emitting Devices

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Received January 11, 1999. Revised Manuscript Received March 29, 1999

New luminescent polymers that contain both electron-withdrawing cyano groups and electron-rich moieties, triphenylamine (TPA) or tetraphenyldiaminobiphenyl (TPD), were synthesized by Knoevenagel condensation of 1,4-bis(cyanomethyl)-2-[(2-ethylhexyl)oxy]-5-methoxybenzene with the dialdehyde of TPA or TPD, respectively. The polymers were characterized by NMR, FT-IR, microanalysis, GPC, DSC, and TGA. Efficient orange photoluminescence was observed with an absolute quantum efficiency of 48% for the TPA incorporated polymer (TPA-CNPPV). Cyclic voltammetry investigation showed that the polymers presented reversible oxidation and reduction with relatively low potentials, which suggested that the polymers have both good electron and hole injection abilities. We demonstrated an effective approach to synthesize polymers with the triad properties of efficient photoluminescence, good hole injection and high electron-affinity properties, which are highly desirable for application in light-emitting devices. This point was supported by the demonstration of a single layer light-emitting device with a configuration of ITO/TPA-CNPPV/Al, in which good external quantum efficiency (0.1%) and bright luminance of 2100 cd/m^2 was achieved. Multilayer LEDs using the polymers as the active layers and different charge injection/transporting layers were also investigated.

Introduction

Conjugated polymers have received increasing attention because of their potential applications as electroluminescent materials for light-emitting devices (LEDs).[1] The ability to customize the luminescent properties of polymers by changing their chemical structures, alongside the feasibility of utilizing simple spin-coating and printing processes for large area display devices, makes organic luminescent polymers very competitive with inorganic luminescent materials. Since the discovery of poly(phenylene vinylene)-based LEDs[2] in 1990, numerous conjugated polymers have been prepared and reported to emit visible light from red,[3] to green,[4] to blue.[5,6] Light emission for these luminescent polymers was produced by the radiational recombination of injected holes and electrons.[7] This implies that the charge injection of electrons and holes, and their appropriate balance are important in achieving good electroluminescence and high quantum efficiency (photons per injected electron). In this context, good charge injection and transporting in conjunction with high luminescence of the material is desired.

For most conjugated luminescent polymers, however, p doping or hole injection is more favorable than n doping or electron injection. This is due to the difficulty in placing electrons into the higher antibonding molecular obitals. Much effort has been made toward the preparation of high electron-affinity polymers which may provide more efficient electron injection properties.[8] The introduction of strong electron affinity groups, e.g. cyano groups, onto a PPV backbone has proved to be an effective way to lower the lowest unoccupied molecular orbital (LUMO) of a polymer and therefore enhanced the electron injection ability.[9] With the enhancement of electron injection of luminescent polymers, air-stable metals such as aluminum can be employed without the loss of electroluminescent efficiency.[10] However, it was noted that a hole injection/transporting

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(1) For references see: Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 402−428. Li, X.-C.; Moratti, S. C. In *Photonic Polymer Systems: Fundamentals, Methods, and Applications*; Wise, D. L., Wnek, G. E., Trantolo, D. J., Cooper, T. M., Gresser, J. D., Eds; Marcel Dekker: New York, 1998; Chapter 10, pp 335−371.

(2) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539−541.

(3) Braun, D.; Heeger, A. J. *Appl. Phys. Lett.* **1991**, *58*, 1982−1984.

(4) Kim, S. T.; Hwang, D. H.; Li, X. C.; Grüner, J.; Friend, R. H.; Holmes, A. B.; Shim, H. K. *Adv. Mater.* **1996**, *8*, 979−982.

(5) Tasch, S.; Niko, A.; Leising, G.; Scherf, U. *Appl. Phys. Lett.* **1996**, *68*, 1090−1092.

(6) Yang, Y.; Pei, Q.; Heeger, A. J. *J. Appl. Phys.* **1996**, *79*, 934−939.

(7) Bradley, D. D. C. *Adv. Mater.* **1992**, *4*, 756−758.

(8) Li, X.-C.; Grimsdale, A. C.; Cervini, R.; Holmes, A. B.; Moratti, S. C.; Yong, T. M.; Grüner, J.; Friend, R. H. *ACS Symp. Ser.* **1997**, *672*, 322−344.

(9) Greenham, N. C.; Moratti, S. C.; Bradley, D. D. C.; Friend, R. H.; Holmes, A. B. *Nature* **1993**, *365*, 628−630.

(10) Moratti, S. C.; Bradley, D. D. C.; Friend, R. H.; Greenham, N. C.; Holmes, A. B. *Mater. Res. Soc. Symp. Proc.* **1994**, *328*, 371−376.

10.1021/cm990018c CCC: $18.00

layer was also needed to offset the poor hole injection of these high electron-affinity luminescent polymers.

Chemically bonded copolymers containing both electron affinity oxadiazoles and electron-donating aromatic amines provided an elegant approach to obtain luminescent polymers with balanced charge injection ability.[11,12] To properly balance the charge injection and transporting ability of a luminescent polymer, it is still of great challenge to choose the right pair of electron-withdrawing/electron-rich moieties. Recently, there have been reports on the use of bipolar pairs of oxadiazole/carbazole[12,13] and oxadiazole/thiophene[14] toward the achievement of "bipolar" or "p−n" luminescent polymers.

We have previously reported a convenient incorporation of cyano/triarylamine, a pair of an excellent electron-withdrawing/electron-rich moieties, into conjugated polymers[15] to achieve desirable properties of luminescence and good electron and hole injection/transporting ability. The synthesis was carried out by using Knoevenagel polycondensation between 1,4-bis(cyanomethyl)-2-[(2-ethylhexyl)oxy]-5-methoxybenzene and the dialdehyde of TPA or TPD, respectively. In this paper, we present our detailed results on synthesis, optoelectronic properties, and electroluminescence of the polymers with various LED configurations. In our comparative study, the TPA incorporated polymer, TPA-CNPPV, possessed the triad properties of efficient photoluminescence, good hole transporting, and high electron-affinity properties. Efficient and bright orange light emission was demonstrated in a single layer LED with air-stable aluminum as cathode. When additional charge transporting layers, or low work function metal (calcium) were employed, higher performance LEDs were achieved.

Experimental Section

Materials. The starting chemicals were purchased from Aldrich Chemical Co. and used as received unless otherwise stated.

2,5-Bis(chloromethyl)-1-methoxy-4-[(2-ethylhexyl)oxy]-benzene (2). To a stirred solution (0−5 °C) of 1-methoxy-4-[(2-ethylhexyl)oxy]benzene (14.7 g, 62.2 mmol) in 1,4-dioxane (300 mL) were added concentrated hydrochloric acid (54 mL) and aqueous formaldehyde (30 mL, 37%). Anhydrous HCl gas was bubbled through the solution for 30 min. The reaction mixture was allowed to warm to room temperature and stirred for 16 h. The reaction mixture was then heated to reflux for 4 h. Cooling back to room temperature, followed by the removal of the solvents in vacuo at 25 °C, gave an off-white waxy residue. The residue was dissolved in ether (200 mL), and the organic phase was washed with water (1 × 50 mL) and dried ($MgSO_4$). The solvent was removed in vacuo at 20 °C. The solid was recrystallized from hexane/methanol at −24 °C. The title compound was filtered, washed with cold methanol, and dried in vacuo at 20 °C to give a white crystalline solid (12.8, 62%): mp 56 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 6.92 (1s, 1H, aromatic H), 6.91 (s, 1H, aromatic H), 4.63 (s, 4H, CH_2Cl), 3.88 (s, 2H, OCH_2), 3.86 (s, 3H, OCH_3), 1.71 (septet, $J = 5.6$ Hz, 1H, CH), 1.62−1.25 (m, 8H, CH_2), 1.02−0.86 (overlapping t, $J = 6$ Hz, 6H, 2 × CH_3); IR (KBr) 2957 s, 2925 s, 2854 s, 1734 w, 1516 s, 1465 s, 1415 s, 1388 m, 1317 m, 1263 s, 1228 s, 1182 m, 1139 m, 1032 s, 971 w, 926 w, 874 m, 733 s, 699 s, 614 s cm^{-1}. Anal. Calcd for $C_{17}H_{26}Cl_2O_2$ C, 61.26; H, 7.86; Cl, 21.27; O, 9.60%. Found: C, 60.9; H, 7.9%.

2,5-Bis(cyanomethyl)-1-methoxy-4-[(2-ethylhexyl)oxy]-benzene (3). Sodium cyanide (0.603 g, 12.3 mmol) was added into the solution of 2,5-bis(chloromethyl)-1-methoxy-4-[(2-ethylhexyl)oxy]benzene (1.574 g, 6.0 mmol) in DMF (40 mL) while stirring. The mixture was heated to 60 °C and stirred for 8 h. After cooling to room temperature, the brown solution was poured into a sodium hydroxide solution (100 mL, 0.1 M) to give a light yellow emulsion which was extracted with chloroform (3 × 100 mL). The organic layer was then washed by water (3 × 70 mL) and dried over sodium sulfate before evaporating the solvent. The crude product was recrystallized from hexane to give a white powder product (1.03 g, 55%): mp 91 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 0.94 (m, 6H), 1.33−1.60 (m, 8H), 1.74 (m, 1H), 3.70 (s, 4H), 3.85 (s, 3H), 3.87 (d, $J =$ 5.5 Hz, 2H), 6.93 (s, 2 H); IR (KBr) 2963 s, 2929 s, 2871 m, 2361 w, 2341 w, 2249 m, 1518 s, 1466 s, 1423 s, 1410 s, 1382 m, 1315 s, 1225 s, 1188 s, 1111 m, 1042 s, 982 w, 938 m, 917 m, 869 s, 837 m, 744 m cm^{-1}. Anal. Calcd for $C_{19}H_{26}N_2O_2$ C, 72.58; H, 8.91; N, 8.91; O, 10.18%. Found: C, 72.7; H, 8.4; N, 8.7%.

***N,N*-Bis(*p*-formylphenyl)phenylamine (7).** The dialdehyde triphenylamine was prepared (yield of 73%) by the Vilsmeier reaction using 10 equiv of $POCl_3$ according to the previously described method:[16] mp 143 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.19 (m, 8H), 7.40 (m, 1H), 7.77 (m, 4H), 9.89 (s, 2H).

4,4′-Bis[(*p*-butylphenyl)phenylamino]biphenyl (9, Bu-TPD). To a solution of tris(dibenzylideneacetone)dipalladium [$Pd_2(dba)_3$] (0.274 g, 1.5 mol % relative to the aniline) and bis-(diphenylphosphino)ferrocene (DPPF) (0.25 g, 2.25 mol % relative to the aniline) in dry toluene (50 mL) under nitrogen was added 4,4′-dibromobiphenyl (3.12 g, 10 mmol) at room temperature, and the resultant mixture was stirred at that temperature for 10 min. Sodium *tert*-butoxide (2.50 g, 26.0 mmol) and aniline (1.82 mL, 20 mmol) were added to this solution and stirred at 90 °C for 4 h. To this solution was added an additional amount of sodium *tert*-butoxide (2.50 g, 26.0 mmol), followed by the addition of 1-bromo-4-butylbenzene (4.26 g, 20 mmol) and toluene (30 mL). The resulting solution was stirred at 90 °C for 24 h. The reaction mixture was cooled to room temperature and poured into water. The mixture was extracted by toluene (3 × 100 mL), and the fractions of organic layers were collected together and concentrated in vacuo to give the crude reaction mixture. Purification of the reaction mixture by flash column chromatography using 8% methylene chloride in hexane afforded the title compound as a white fluffy solid: yield 55%; mp 133 °C; ^1H NMR (300 MHz, CD_2Cl_2) δ 0.95 (t, $J = 7.3$ Hz, 6H), 1.40 (m, 4H), 1.58 (m, 4H), 2.59 (t, $J = 7.7$ Hz, 4H), 6.92−7.21 (m, 10H), 7.24 (d, $J = 8.4$ Hz, 2H), 7.27 (d, $J = 8.4$ Hz, 2H), 7.44 (d, $J = 8.3$ Hz, 2H), 7.45 (d, $J = 8.3$ Hz, 2H).

4,4′-Bis[(*p*-butylphenyl)(*p*-formylphenyl)amino]biphenyl (Dialdehyde BuTPD, 10). To the mixture of **9** (1.29 g, 2.150 mmol), 1,2-dichloroethane (6 mL), DMF (0.377 mL, 2.3 equiv) was added $POCl_3$ (0.479 mL, 2.4 equiv to **9**) under nitrogen. The dark brown suspension was heated to reflux overnight (16 h), and then cooled to room temperature. The black solution was pored into a sodium acetate aqueous solution (4.0 g NaOAc in 100 mL H_2O), and stirred for 1 h at room temperature. The dark green solution was extracted with CH_2Cl_2 (4 × 70 mL). The organic layer was washed with water (2 × 70 mL), dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by flash chromatography on silica eluting with EtOAC/hexane (1:6 to 1:1, v/v) to give a yellow powder product **10** (0.88 g, 63%): ^1H NMR (300 MHz, CD_2Cl_2) δ 0.96 (t, $J = 7.6$ Hz, 6H), 1.41 (dd, $J = 7.3$ Hz, 4H), 1.60 (dd, $J = 7.3$ Hz, 4H), 2.63 (t, $J = 7.6$ Hz, 4H), 7.03 (d, $J = 8.3$ Hz, 4H), 7.11 (d, $J = 8.2$ Hz, 4H), 7.20 (m, 8H), 7.57 (d,

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(11) Kido, J.; Harada, G.; Nagai, K. *Chem. Lett.* **1996**, 161−162.

(12) Boyd, T. J.; Geerts, Y.; Lee, J. K.; Fogg, D. E.; Lavoie, G. G.; Schrock, R. R.; Rubner, M. F. *Macromolecules* **1997**, *30*, 3553−3559.

(13) Peng, Z. H.; Bao, Z. N.; Galvin, M. E. *Chem. Mater.* **1998**, *10*, 2086−2090.

(14) Yu, W. L.; Meng, H.; Pei, J.; Huang, W.; Li, Y. F.; Heeger, A. J. *Macromolecules* **1998**, *31*, 4838−4844.

(15) Li, X.-C.; Jen, A. K.-Y.; Liu, Y.-Q.; Liu, S.; Bharathan, J.; Cahng, S.-C.; Yang, Y. *ACS Polym. Prepr.* **1998**, *93* (2), 1093−1094.

(16) Rost, H.; Teuschel, A.; Pfeiffer, S.; Hörhold, H. H. *Synth. Met.* **1997**, *84*, 269−270.

$J = 7.9$ Hz, 4H), 7.67 (d, $J = 8.3$ Hz, 4H); MS (CI, MH^+) 657.5 (657.3 calcd for $C_{46}H_{45}N_2O_2$).

TPA-CNPPV 11. Tetrabutylammonium hydroxide (62 μL, 1.0 M in methanol) was added into the degassed mixture solution of the dinitrile **3** (0.2174 g, 0.6912 mmol), the dialdehyde **7** (0.2083 g, 0.6912 mmol), THF (3 mL), and *tert*-butyl alcohol (6 mL). The yellow solution turned green and was heated to 50 °C while stirring under nitrogen atomosphere. After stirring for 2 h, the dark green mixture was poured into methanol (80 mL), and the precipitate was collected by filtration. The crude orange red polymer was Soxhlet extracted with THF to remove the insoluble part of the polymer. The polymer solution was concentrated to ∼15 mL and poured into methanol (200 mL) to give the polymer precipitate. After filtration and drying under vacuum, orange red polymer **11** was obtained (0.24 g, 60%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.86 (br, 6H), 1.28, 1.46 (2, 8H), 1.75 (br, 1H), 3.81 (br, 2H), 3.93 (br, 5H), 6.8−7.4 (m, 13H), 7.4−8.0 (m, 4H); IR (film on KBr) 2950 m, 2930 m, 2858 m, 2208 m, 1685 w, 1585 s, 1501 s, 1322 m, 1282 m, 1214 m, 1020 m, 799 w, 692 w cm^{-1}; GPC assay $M_w = 48\,800$; polydispersity index 1.7. Anal. Calcd for $C_{39}H_{37}N_3O_2$ C, 80.79; H, 6.45; N, 7.25%. Found: C, 79.3; H, 6.6; N, 6.9%.

TPD-CNPPV 12. The preparation procedure was similar to **11**. An orange red polymer **12** was obtained (0.20 g, 50%): ^{1}H NMR (300 MHz, CD_2Cl_2) δ 0.93 (br, 12H), 1.4 (br, 10H), 1.6 (br, 6H),2.6 (br, 4H), 3.7−3.9 (2 br, 5H), 7.1−7.8 (m, 28H); IR (film on KBr) 2926 m, 2857 w, 1519 s, 1495 s, 1461 m, 1324 m, 1213 m cm^{-1}; GPC assay $M_w = 20\,100$; polydispersity 1.8. Anal. Calcd for $C_{65}H_{66}N_4O_2$ C, 83.46; H, 7.13; N, 5.99%. Found: C, 81.8; H, 7.1; N, 5.3%.

Characterization. NMR spectra were recorded on a Varian WM-300 (300 MHz) spectrometer using deuterio solvent as reference or internal deuterium lock. The chemical shift data for each signal were given in units of δ relative to tetramethylsilance (TMS) where δ (TMS) = 0. Differential scanning calometry (DSC) and thermal gravimetric analysis (TGA) for the polymers were carried out under nitrogen at a rate of 10 °C per minute using the Shimadzu instrument. FT-IR spectra were recorded on an infrared spectrometer (Nicolet 210). UV−vis spectra were recorded on a Perkin-Elmer spectrophotometer (Lambda 9 UV/vis/NIR). Gel permeation chromatography (GPC) measurements were carried out using a Waters Styragel (HR 4E, 7.8 × 300 mm) column with polystyrene as the standard, and THF as the solvent.

Cyclic voltammogramms of the polymer films (spin-coated onto indium−tin oxide coated glass, ITO glass) were recorded at room temperature in a typical three electrode cell with a working electrode (ITO glass), a reference electrode (Ag/Ag^+, externally referenced against Fc/Fc^+, 0.21 V), and a counter electrode (Pt gauze) under a nitrogen atmosphere at a sweeping rate of 40 mV/s (CV-50W Voltammetric analyzer, BAS). A solution of tetrabutylammonium perchlorate (TBAP) in anhydrous acetonitrile was used as the electrolyte.

LEDs Fabrication and Measurement. For the single-layer devices, polymer solutions in toluene (1% g/mL) were used to spin-cast on top of the anodic electrode, ITO glass (100 Ω/diameter, Delta Techn. Ltd.). For the double-layer devices, a hole injection poly(*N*-vinyl carbazole) (PVK) (M = 1000 kDa) layer (50 nm) was first spin-cast onto ITO glass using chloroform as the solvent (0.8% g/mL), or a hole injection layer of copper phthalocyanine (CuPc, purified by twice sublimation in vacuo) was evaporated onto ITO glass under vacuum (2×10^{-6} mba) and heating conditions, followed with the spin-casting of the active polymer in toluene. For the triple layer devices, 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) (2% g/mL solution in acetone) was further spin-cast on top of the active polymer layer to form an electron injection and hole blocking layer (50 nm). The cathode Al electrode (∼200 nm) was deposited by thermal evaporation under vacuum (2×10^{-6} mbar). The film thickness was measured with a Dektak surface profilometer (Model 3030). The active emissive area defined by the cathode was about 8 mm^2. All of the devices were made and encapsulated (with adhesive tape) in an argon-filled glovebox.

Photoluminescent spectra of the neat films (coated on quartz glass) or solutions of the polymers were recorded by a CCD system (Instaspec IV CCD, Oriel) under UV light excitation (366 nm). Electroluminescence spectra of LEDs were recorded with the same CCD system. The absolute PL quantum efficiency of the polymer thin films (coated on quartz glass of 1 cm^2 area) were measured based on the published method[17] in a full reflection integration sphere (ϕ = 4 in., Newport). $I-V-L$ curves of the LEDs were recorded by a semiconductor analyzer (4155B semiconductor parameter analyzer, Hewlett-Packard) with a calibrated multifunctional optical meter (model 2835-c, Newport).

Results and Discussion

Synthesis and Characterization. The synthesis of the polymers was accomplished by using Knoevenagel polycondesation condition,[18,19] which requires the use of an aryl dialdehyde monomer and an aryl bismethylene nitrile monomer. To render solubility of the conjugated polymers in common organic solvents, the dinitrile monomer **2** with a long flexible alkoxyl substituent, 2-ethylhexyloxy, was prepared starting from 4-methoxylphenol (Scheme 1). We chose the dialdehydes of two typical triarylamines, namely triphenylamine (TPA) and tetraphenyldiaminobiphenyl (TPD) as the hole injecting/transporting chromophores. Both TPA and TPD have been widely used as efficient hole transport layers for organic LEDs, owing to their ability to form aminium radical cations,[20] and their high hole mobilities.[21,22] Hole transport polymers containing aromatic amines[23,24] and electroluminescent polymers with aromatic amines[16,25] have been recently reported in the use of polymer LEDs. The dialdehyde monomer **7** could be obtained by a two-step reaction procedure starting from triphenylamine as shown in Scheme 1. Direct double formylation of TPA by the Vilsmeier reaction proved to be difficult due to the deactivation effect of the first carbonyl group on TPA, and mainly gave monoformylated TPA **6** under normal stoichiometry of $POCl_3$/DMF (up to 3.5 equiv $POCl_3$/DMF). With a large excess of $POCl_3$/DMF (∼10 equiv), the diformylated TPA **7** was produced with a good yield (73%). Modified TPD **9** with two *n*-butyl substituents on the molecule was obtained by a one-pot procedure using a modified Bachwald reaction, [26,27] where dibromobenzidine and 4-butyl-bromobenzene were sequentially added to aniline in the presence of a palladium catalyst (Scheme 1). By using the Vilsmeier reaction, **9** was readily converted into the dialdehyde

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[17] Greenham, N. C.; Samuel, I. D. W.; Hayes, G. R.; Phillips, R. T.; Kessener, Y. A. R. R.; Moratti, S. C.; Holmes, A. B.; Friend, R. H. *Chem. Phys. Lett.* **1995**, *241*, 89−96.

[18] Moratti, S. C.; Bradley, D. D. C.; Cervini, R.; Friend, R. H.; Greenham, N. C.; Holmes, A. B. *SPIE Proc.* **1994**, *2144*, 108−114.

[19] Kim, D.-J.; Kim, S.-H.; Zyung, T.; Kim, J.-J.; Cho, I.; Choi, S. K. *Macromolecules* **1996**, *29*, 3657−3660.

[20] Louie, J.; Hartwig, J. F.; Fry, A. J. *J. Am. Chem. Soc.* **1997**, *119*, 11695−11696.

[21] Adachi, C.; Tokito, S.; Tsutsui, T.; Saito, S. *Jpn. J. Appl. Phys.* **1988**, *27*, 59.

[22] Kido, J.; Agai, K.; Ohashi, Y. *Chem. Lett.* **1990**, 657−659.

[23] Kido, J.; Harada, G.; Komada, M.; Shionoya, H.; Nagai, K. *ACS Symp. Ser.* **1997**, *672*, 381−394.

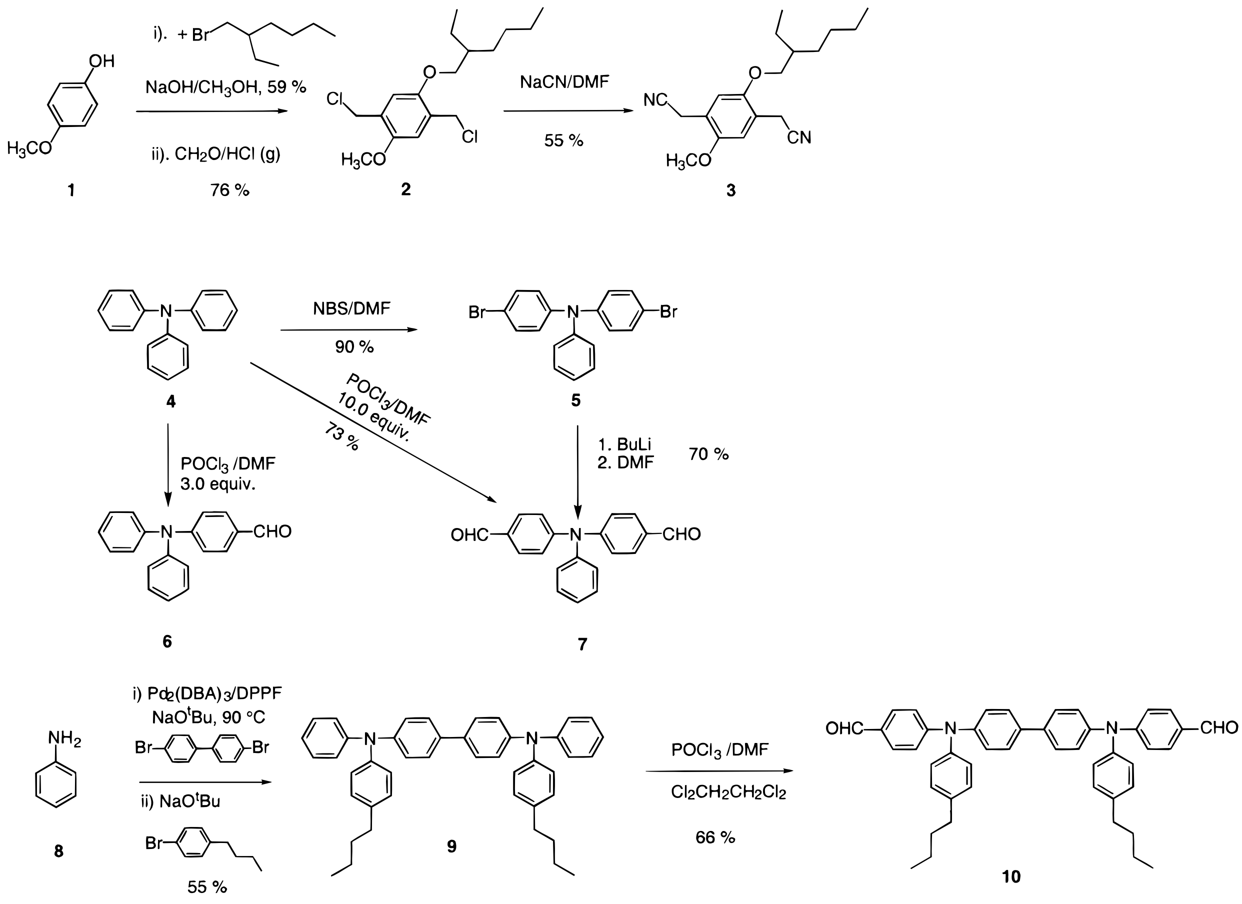
[24] Bellmann, E.; Shaheen, S. E.; Thayumanavan, S.; Barlow, S.; Grubbs, R. H.; Marder, S. R.; Kippelen, B.; Peyghambarian, N. *Chem. Mater.* **1998**, *10*, 1668−1676.

[25] Liu, Y.; Liu, M. S.; Li, X.-C.; Jen, A. K. Y. *Chem. Mater.* **1998**, *10*, 3301−3303.

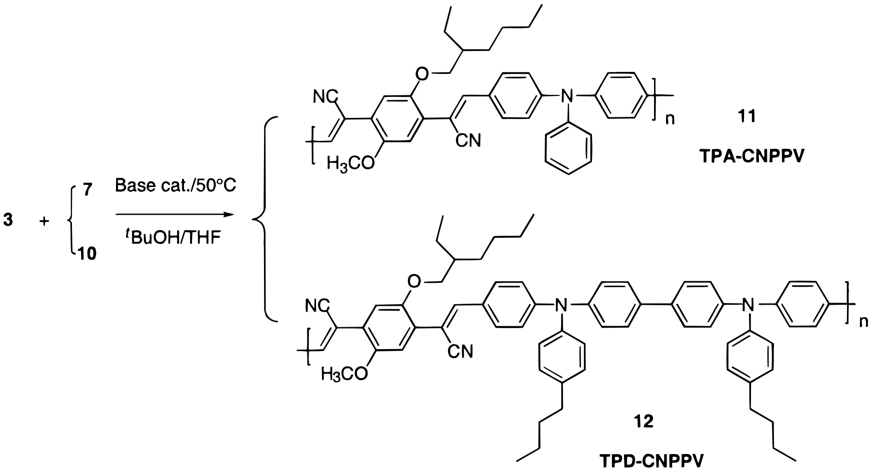
[26] Marcoux, J. F.; Wagaw, S.; Buchwald, S. L. *J. Org. Chem.* **1997**, *62*, 1568−1569.

[27] Thayumanavan, S.; Barlow, S.; Marder, S. R. *Chem. Mater.* **1997**, *9*, 3231−3235.

Scheme 1. Synthesis of Monomers



Scheme 2. Synthesis of Polymers via Knoevenagel Condensation Reaction



TPD monomer **10** with a good yield. Here, the two *n*-butyl groups significantly enhanced the solubility of the conjugated polymer, as our result showed that the analogous polymer of **12** but without the *n*-butyl substituent was barely soluble in conventional organic solvents.[15]

Under a basic condition, the polymerization between **7** or **10** and **3** was generally fast and straightforward (Scheme 2). However, prolonged reaction time could lead to an insoluble gel, which was probably the cross-linking products from the Michael reaction. Polymer **11** was an orange red powder and **12** was an orange powder. Both polymers were soluble in conventional organic solvents, such as tetrahydrofuran, chloroform, and toluene. Gel permeation chromatography measurements revealed the molecular weight for **11** ($M_w = 48\,800$, polydispersity index 1.7) and for **12** ($M_w = 20\,100$, polydispersity index 1.8). Measurements of differential scanning calometry (DSC) and thermal gravimetric analysis (TGA) showed that both **11** and **12** were stable up to 290 °C, but started to degradate after 300 °C due to thermal oxidation (Figure 1). DSC measurements revealed a glass transition temperature of 159 °C for **11** and 154 °C for **12**. No melting points were observed for the polymers before thermal decomposition.

Optoelectronic Properties of the Polymers. Both polymers fluoresced orange-red under the irradiation of long UV light (366 nm). Figures 2 and 3 show the UV

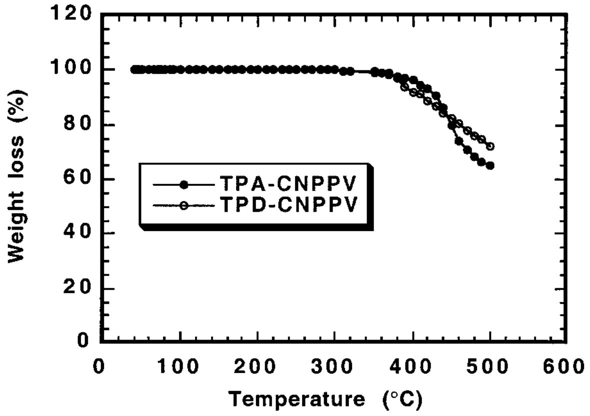


Figure 1. Thermal gravimetric analysis (TGA) of polymer **11** and **12** (under nitrogen atomosphere at 40 °C/min).

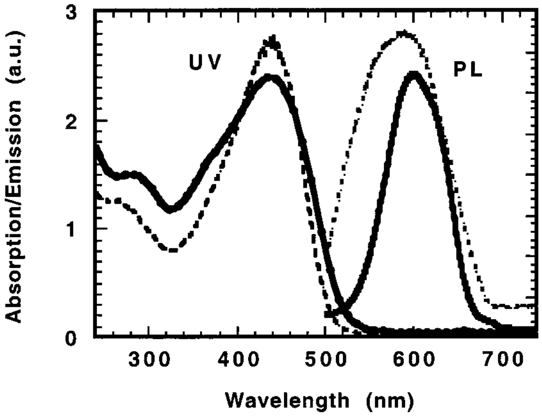


Figure 2. UV−vis, PL spectra for TPA-CNPPV (**11**) in solid (solid lines) and in solution (dotted lines, CH_2Cl_2).

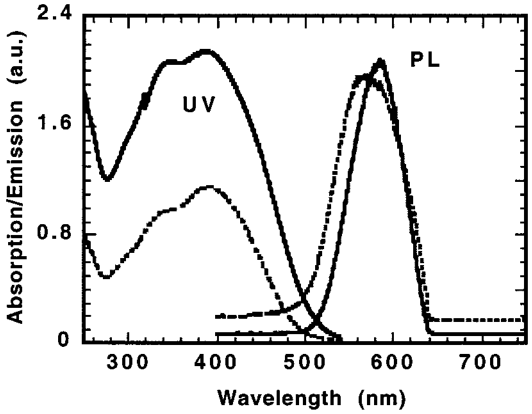


Figure 3. UV−vis and PL spectra for TPD-CNPPV (**12**) in solid (solid lines) and in solution (dotted lines, CH_2Cl_2).

and photoluminescent spectra of **11** and **12**, respectively. There was a slight blue-shift of the emission maxima for both polymers when in solution compared to that of the solid state. The emission peak position for **11** was located at 600 nm (film) and for **12** at 590 nm (film). A Stokes shift of 160 nm for **11** and 200 nm for **12** were observed. Mirror images between UV and PL spectra were normally found for both of the polymers. The quantum efficiencies of photoluminescence, as measured in an integration sphere for the neat polymer film,[17] were measured to be 48% for **11** and 17% for **12**, which were higher than that of poly[5-methoxy-2-[(2-ethylhexyl)oxy]phenylene vinylene] (MEH-PPV, 12−15%). This implies that the combination of an electron-withdrawing cyano group with the electron-donating triarylamine can lead to bright photoluminescent polymers. In the same way, we made a conjugated polymer by Knoevenagel polycondesation of **3** and a bisthiophene dialdehyde monomer. However, the polymer appeared purple and was nonfluorescent, probably due to a strong intramolecular charge transfer from the bisthiophene to the cyano group. We further examined the PL quantum efficiency stability under continuous UV irradiation. The PL efficiencies of the polymers were found to drop by about 40% after 7 h UV irradiation. For instance, the PL quantum efficiency of **11** remained at 30% after the test.

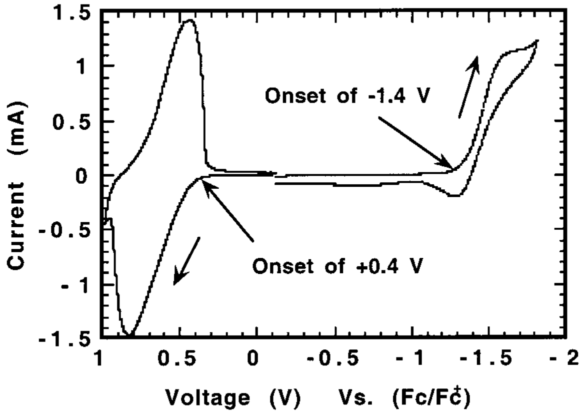


Figure 4. Cyclic voltammogram of polymer **11** film coated on ITO glass. (Measured in acetonitrile solution of TBAP (0.1 M) at 40 mV/s, referenced vs Ag/Ag^+ and calibrated externally vs Fc/Fc^+ 0.21 V).

To get information on the charge injection for **11** and **12**, redox measurements of the polymer thin films (coated on ITO glass) were recorded using cyclic voltammetry. Both polymers possessed reversible oxidation peaks at relatively low potentials when swept anodically. The onset of the oxidation for **11** was located at 0.4 V and for **12** at 0.5 V, which were lower than that for PPV (0.85 V) and for CN-PPV (1.0 V).[8] Since the oxidation process for a conjugated polymer in an electrochemical cell is closely related with the removal of electrons (or the injection of the holes) from the HOMO of the material, the lower oxidation potentials for **11** and **12** suggest a better hole injection ability. In terms of anodic reversibility, our polymers presented better hole injection ability than the reported oxadiazole/carbazole[13] or oxadiazole/thiophene[14] bipolar polymers. The improved hole injection ability for **11** and **12** were attributed to the incorporation of TPA or TPD moieties. When swept cathodically, quasi-reversible reduction peaks were observed for both **11** and for **12**. Figure 4 shows the full scan cyclic voltammogram for **11**. The onset of the reduction potential for **11** was located at −1.4 V and for **12** at −1.65 V, which were higher than that of PPV (−1.7 V).[28] Accordingly, the reduction process for a conjugated polymer in an electrochemical cell is related with the electron capture ability (or electron injection ability). It is therefore reasonable to infer that polymers **11** and **12** have higher electron affinity than their parent polymer, PPV, owing to the electron-withdrawing cyano groups in the polymers.

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(28) Li, X.-C.; Kraft, A.; Cervini, R.; Spencer, G. C. W.; Cacialli, F.; Friend, R. H.; Grüner, J.; Holmes, A. B.; De Mello, J. C.; Moratti, S. C. *Mater. Res. Soc. Symp. Proc.* **1996**, *413*, 13−22.

Table 1. Optical and Electronic Parameters for 11 and 12

	λ_{max} (nm)	E_g (eV)	E_{ox} (V)	E_{red} (V)	HOMO (eV)	LUMO (eV)
11	440	2.4	0.7	−1.5	−5.5	−3.3
12	390	2.4	0.6	−1.8	−5.4	−3.0

[a] $\pi-\pi^*$ band gap E_g was calculated from the onset of UV absorption (film). E_{ox} and E_{red} were the average value between their corresponding redox peaks.

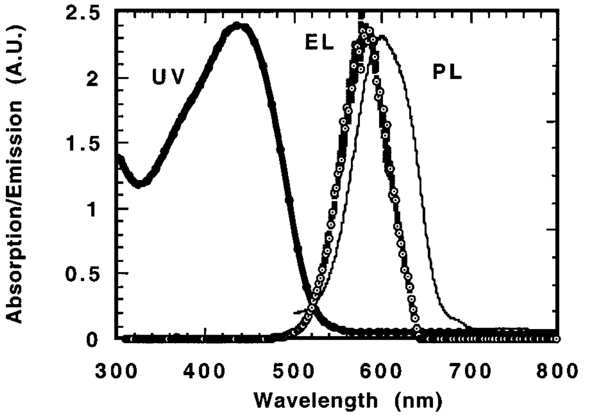

Figure 5. Electroluminescent spectrum of **11** (ITO/**11**/Al) and its comparison with UV and PL spectra.

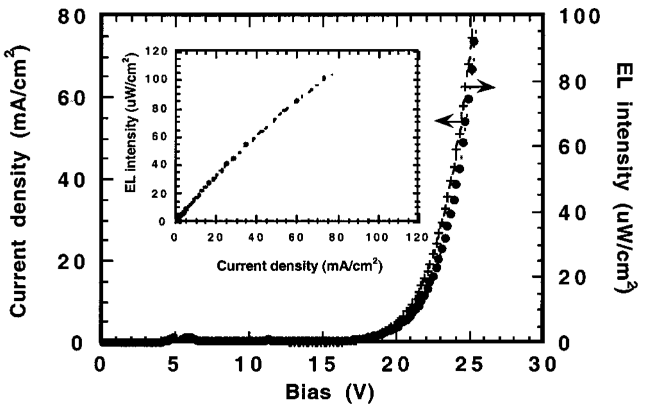

Figure 6. *I*−*V*−*L* curve for the device of ITO/**11**/Al.

Table 2.[a] **LED Device Structures and External Quantum Efficiencies for TPA-CNPPV (11) and TPD-CNPPV (12)**

device	ITO/P/Al	ITO/PVK/P/Al	ITO/CuPc/P/Al	ITO/PVK/P/Ca
ϕ_{ext}(%) P = **11**	0.1	0.04	0.01	0.15
ϕ_{ext}(%) P = **12**	0.02	0.022	0.007	0.034

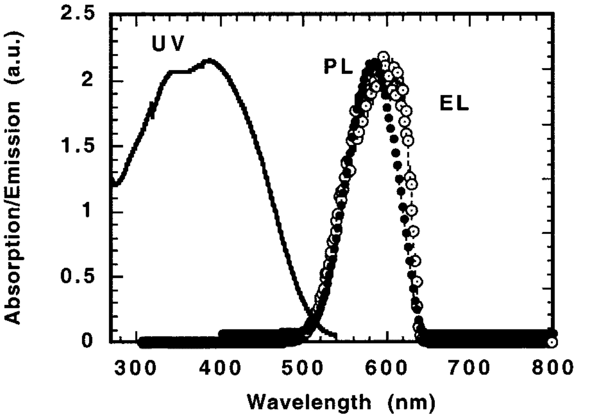

Figure 7. Electroluminescent spectrum of **12** (ITO/PVK/**12**/Al) and its comparison with UV and PL spectra.

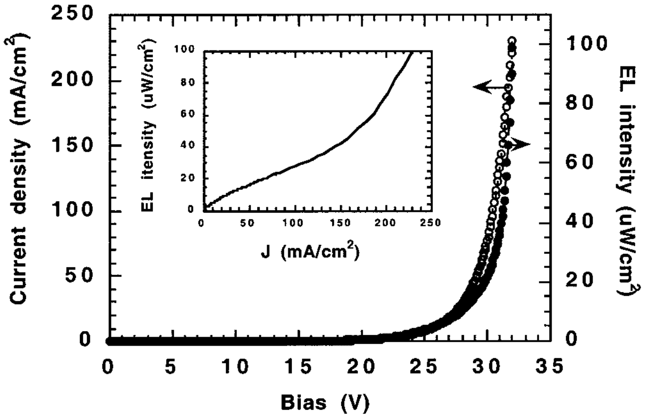

Figure 8. *I*−*V*−*L* curve for the device of ITO/PVK/**12**/Al.

According to the redox peak positions of the CV measurements the HOMO/LUMO positions for **11** and **12** were estimated based on the reference energy level of ferrocene (4.8 eV below the vacuum level).[29] As it is revealed from Table 1 that the band gaps, obtained from the HOMO/LUMO positions, are close to those calculated from the electronic absorption spectra. Care should be taken when comparing the HOMO/LUMO positions derived from cyclic voltammetric measurements with the ones from other measurements. Recent studies show that the HOMOs of several hole transporting/emitting compounds obtained by ultraviolet photoelectronscopy (UPS) were 0.3−0.6 eV lower than that obtained by cyclic voltammetry.[30] Nevertheless, the CV measurement and related HOMO/LUMO position judgment provide a convenient and useful quantitative comparison for the charge injection ability of conjugated polymers. The CV data for many luminescent polymers and charge transporting polymers have been well-documented in recent years.[8,13,31,32] Besides, the inonization potential and the electron affinity of a conjugated material can also be judged by using CV redox data.[33,34]

Electroluminescent Properties. To investigate the electroluminescent properties of the polymers, various LEDs with different configurations were fabricated and evaluated. For polymer **11**, a single layer device of ITO/**11**(100 nm)/Al was made initially. Bright orange electroluminescence was observed under normal day lighting condition. Figure 5 shows the electroluminescence spectrum, in comparison with the UV−vis and PL spectra in neat films of the polymer. The EL spectrum resembled its PL spectrum, suggesting that the same excited state, called singleton, was responsible for both EL and PL emission. The device turn-on voltage was

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(29) Pommerehne, J.; Vestweber, H.; Guss, W.; Mahrt, R. F.; Bässler, H.; Porsch, M.; Daub, J. *Adv. Mater.* **1995**, *7*, 551−554.

(30) Anderson, J. D.; McDonald, E. M.; Lee, P. A.; Anderson, M. L.; Ritchie, E. L.; Hall, H. K.; Hopkins, T.; Mash, E. A.; Wang, J.; Padias, A.; Thayumanavan, S.; Barlow, S.; Marder, S. R.; Jabbour, G. E.; Shaheen, S.; Kippelen, B.; Peyghambarian, N.; Wightman, R. M.; Armstrong, N. R. *J. Am. Chem. Soc.* **1998**, *120*, 9646−9655.

(31) Yamamoto, T.; Sugiyama, K.; Kushida, T.; Inoue, T.; Kanbara, T. *J. Am. Chem. Soc.* **1996**, *118*, 3930−3937.

(32) Jandke, M.; Strohriegl, P.; Berleb, S.; Werner, E.; Brutting, W. *Macromolecules* **1998**, *31*, 6434−6443.

(33) Brédas, J. L.; Silbey, R.; Boudreaux, D. S.; Chance, R. R. *J. Am. Chem. Soc.* **1994**, *105*, 6555.

(34) Janietz, S.; Bradley, D. D. C.; Grell, M.; Giebeler, C.; Inbasekaran, M.; Woo, E. P. *Appl. Phys. Lett.* **1998**, *73*, 2453−2455.

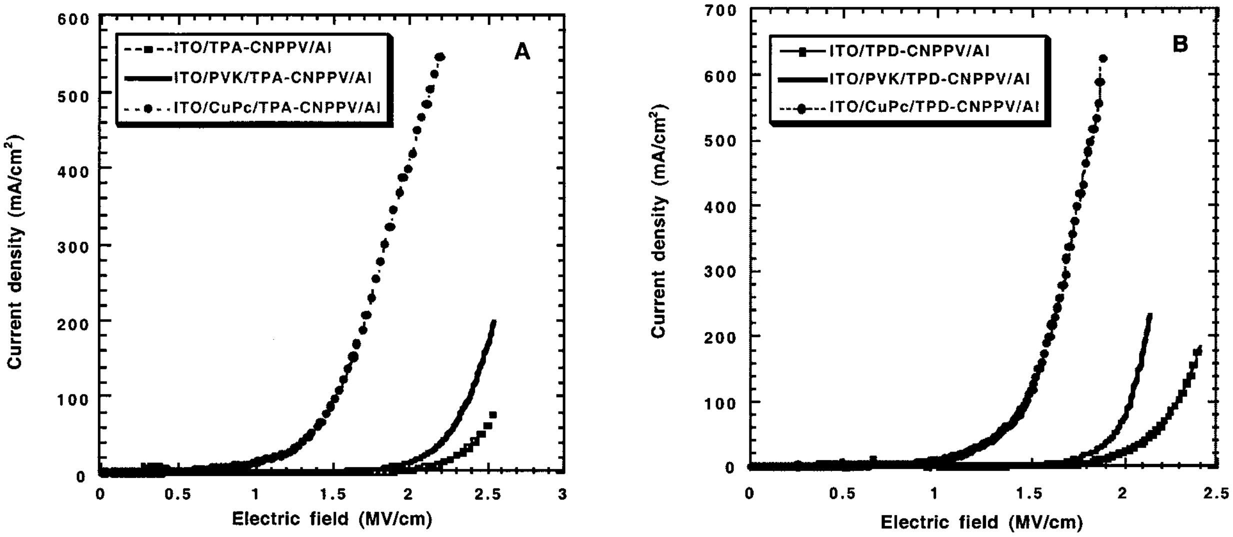

Figure 9. The relatioship between the electric field and current density for various LEDs.

13 V (defined as the voltage from which EL light can be detected), and a maximal external quantum efficiency of 0.1% (photons per electron) was measured at 20.9 V with a current density of 6.25 mA/cm^2. The quantum efficiency is higher than normal single layer polymer LEDs using aluminum as cathode. For instance, the quantum efficiency of MEH-PPV single layer devices is normally less than 0.01%. Although the working lifetime of the device was not investigated systematically, we noticed that the device remained functioning after 1 week even simply using polyethylene adhesive tape as the encapsulating cover. The $I-V-L$ curve, as shown in Figure 6, characterized the properties among the current (I), bias voltage (V), and the electroluminescence output (L). The inset of Figure 6 shows that the EL output is linearly proportional to the injected current density. The highest luminance, before breaking the device, for the single layer device was measured to be 146.4 μW/cm^2 at 27 V with a current density of 166.8 mA/cm^2. This corresponds to a peak luminance of 2100 cd/m^2 with an external quantum efficiency of 0.05% (here we use the spectral luminous efficacy $K_{585} = 500$ lm/W). This brightness is quite high for aluminum based single-layer polymer LEDs.

Double-layer devices with a hole transporting layer was also fabricated to investigate the device performance with the influence of charge transporting/injecting layers. For the device of ITO/PVK/**11**/Al, bright orange light emission was readily observed under a forward bias condition, and more reproducible LEDs could be obtained. The trun-on voltage of the double-layer devices roughly remained the same. However, a drop of external quantum efficiency (0.04% for ITO/PVK/TPA-CNPPV) was normally observed in comparison to the single-layer device. This may suggest that PVK actually played a role as a good buffer layer which may offset uneven surface problems on the ITO, or to prevent possible pinholes in the emissive layer. On the other hand, it may also be inferred that TPA-CNPPV has a good enough hole injection ability. Further enhancement of hole injection leads to unbalanced charge injection, thus lowering the device efficiency. This point was also apparent when using copper phthalocyanine (CuPc) as a hole tranporting layer, and the device ITO/CuPc/TPA-CNPPV/Al showed an even lower external quantum efficiency (0.01%).

When replacing aluminum with calcium, a lower work function metal (2.9 eV), an improved external quantum efficiency of 0.15% was achieved with the device configuration of ITO/PVK (50 nm)/**11** (80 nm)/Ca. However, calcium is an air-sensitive metal and the devices with calcium under our encapsulation condition were less stable. Table 2 summarizes the device structures and their external quantum efficiencies.

Similar experiments of the LEDs with TPD-CNPPV as active material were also carried out. The devices showed orange light emission with the peak position located at 598 nm (Figure 7). Although similar brightness was achieved with the TPD-CNPPV based LEDs, the devices of **12** were generally less efficient than that of **11** (Table 2). Figure 8 shows the $I-V-L$ characteristics of a double layer device, ITO/PVK/**12**/Al. In comparison to Figure 6, a larger current density is needed to achieve similar EL light output. We observed "heating" phenomenon of the devices while they were working at large current density. The inset of Figure 8 shows a steeper increase of EL output at larger current density (>150 mA/cm^2). Whether or not the steeper EL increase is related with the temperature increase of the device is still under investigation. We also tried to use a triple-layer device in which PVK was used as hole injection and buffer layer and PBD was used as electron injection and hole blocking layer; however, our results suggested no apparent improvement of efficiency for TPD-CNPPV. This may be attributed to the relatively lower PL quantum efficiency of TPD-CNPPV compared with TPA-CNPPV.

The turn-on voltage of the LEDs for both polymers could be reduced if the thickness of the active layer was reduced. However, the inherent threshold electric field would remain the same. With the reduction of thickness of the active layer, the chances of pinholes formation would be increased, which would lead to device failure. The most efficient way to lower the turn-on voltage that we have found was to employ one or two charge injection layer(s) and construct a multilayer LED. Figure 9 shows that the turn on electric field for multilayer devices were effectively reduced. Therefore, large current injection and considerably lower turn-on voltage (around 7 V) were achieved for the devices using copper phthalocyanine (CuPc) as a hole injection layer. Although bright LEDs could be achieved with the CuPc as hole transporting layer, the device quantum efficiency was normally reduced, probably due to the excessive hole injection into the polymers. We believed that there should be a balance between the reduction of turn-on voltage and the sacrifice of device quantum efficiency if carefully choosing appropriate thinkness of hole transporting layers. It is worth mentioning that a blue shift of EL spectrum of about 18 nm was also observed with CuPc as a hole transporting layer, owing to the absorbance of CuPc in the orange light region.

Conclusions

New soluble luminescent polymers were prepared by Knovenagel condensation of 1,4-bis(cyanomethyl)-2-[(2-ethylhexyl)oxy]-5-methoxybenzene with the dialdehyde of TPA and TPD, respectively. These polymers possessed the triad properties of bright photoluminescence, good hole injection and high electron-affinity properties. The combination of these properties is highly desirable for the applications in organic light-emitting devices. Bright orange electroluminescence with a peak luminance of 2100 cd/m^2 was achieved for both of the polymers. Due to its high photoluminescence efficiency (48%), the TPA-CNPPV based LEDs were generally more efficient than the TPD-CNPPV based LEDs. A single-layer device that used TPA-CNPPV as the active layer and aluminum as the cathode showed a high external quantum efficiency (0.1%). When hole transporting layers were employed, the turn-on electric field of the LEDs was reduced effectively. With the use of low work function metal as cathode, and with further optimization on the device fabrication, better device performance with higher quantum efficiency is possible.

Acknowledgment. Financial support from the Office of Naval Research (ONR) through the MURI Center (CAMP) and the Air Force Office of Scientific Research (AFOSR) through the DURIP program is gratefully acknowledged. We thank Dr. Yang Yang (UCLA), Dr. Jianyao Wu, and Mr. Craig Urian for their interest in this work.

CM990018C