View Article Online / Journal Homepage / Table of Contents for this issue

JOURNAL OF Materials CHEMISTRY

Synthesis and characterization of a new conjugated polymer containing cyano substituents for light-emitting diodes

Xia Wu, Yunqi Liu* and Daoben Zhu*

Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China. E-mail: liuyq@infoc3.icas.ac.cn.

Received 23rd October 2000, Accepted 7th February 2001
First published as an Advance Article on the web 22nd March 2001

Published on 22 March 2001. Downloaded by University of Michigan Library on 21/10/2014 20:56:10.

A new luminescent conjugated polymer (CN-P3PV) containing cyano groups as electron transporting units was synthesized by a Suzuki coupling reaction. CN-P3PV was characterized by ^{1}H NMR, FT-IR, GPC, DSC, and TGA. The synthesized polymer possessed high thermal stability ($T_d = 360\,°C$, $T_g = 151\,°C$), high electron affinity, and good thin-film forming ability. Electrical characterization of a double-layer organic LED based on the structure of ITO/CuPc/CN-P3PV/Ca/Ag showed high electron transporting ability and good electroluminescence performance with the emission of bright orange light.

Introduction

Since the first report by Cambridge group in 1990 on electroluminescence (EL) in a polymer light-emitting diode (LED),[1] a great variety of polymers with different color emission,[2–4] electron affinities,[5,6] ionization potentials[7,8] and photoluminescence (PL) efficiencies have been synthesized, and their EL properties have also been extensively studied. Light emission from a polymer LED is produced in the luminescent polymer layer *via* recombination of electrons and holes from two electrodes. The basic requirements for the organic layer are that it should luminesce efficiently and be a good charge transporter, and it must be capable of undergoing efficient charge transfer to an electrode.[9] The EL emission efficiency is high on the balanced injection of the charges from the respective electrodes.[10,11] However, for the majority of conjugated polymers investigated, electron injection has proved to be more difficult than hole injection, because organic materials and polymers tend to have low electron affinities. This has been largely remedied by the use of metals with a low work-function (especially Ca) as the cathode material. However, calcium is highly susceptible to atmospheric degradation.[12] To circumvent these problems, several strategies have been utilized, such as, using multilayer structures with one or more charge transporting layers,[13,14] and blending small molecules into a polymer matrix.[15] These methods have been very successful.

Because electrical and optical properties (*e.g.* color and emission efficiency) of conjugated polymers can be tailored by manipulation of their chemical structures, the improvement of EL devices requires optimization of not only the structure of the device but also the chemical structure of the electroluminescent polymer, and recently synthetic design has become a vital component in the optimization of polymer LEDs.[16,17] We have been investigating polymers with balanced charge injection by increasing the electron affinity of the polymer. The introduction of strong electron affinity groups,[18,19] *e.g.* cyano, oxadiazole, halide, methylsulfinyl or trifluoromethyl groups, onto a poly(*p*-phenylenevinylene) (PPV) backbone has proved to be an effective way to lower the LUMO (to shift away from the vacuum level) of a polymer and therefore enhance the electron injection ability. With the enhancement of electron injection of luminescent polymers, air-stable metals such as aluminium can be employed without the loss of electroluminescent efficiency.

We report a new cyano-containing polymer, CN-P3PV, which can be recognized as a CN-PPV derivative,[18] with two less vinylene linkages for every four vinylene groups. The number of CN substituents and vinylene groups is half that of the CN-PPV reported by the Cambridge group.[18] The cyano group,[19] an excellent electron-transporting moiety, is introduced into the conjugated polymer to achieve desirable properties of luminescence and good electron injection/transporting ability. The hexyloxy side groups in the repeat unit can enhance the solubility of the resulting polymer, and therefore enhance the processability and quality of the thin film in LED devices. The solubilizing side groups on the phenyl groups twist the replaced phenylene rings considerably out of plane and confine the rotation to the bonds that link the aromatic ring systems. This drastically decreases the interaction of the aromatic π-electron system, so that the polymer should have a higher glass-transition temperature (T_g). In this paper, we present our detailed results on synthesis, optoelectronic properties, and electroluminescence of the polymer.

Results and discussion

Synthesis and characterization

A copolymer containing cyano groups was prepared with the Suzuki coupling reaction,[20] from the dibromo-terminated phenylenevinylene monomer (**1**) and the diboronic acid (**2**) followed by hydrolysis in the presence of aqueous HCl. The synthetic route to this copolymer is illustrated in Scheme 1.

The reaction of 4-bromophenylacetonitrile and terephthalaldehyde easily occurred to produce 1,4-bis(β-cyano-*p*-bromostyryl)benzene, monomer **1**, in over 95% yield using NaOH as the base.

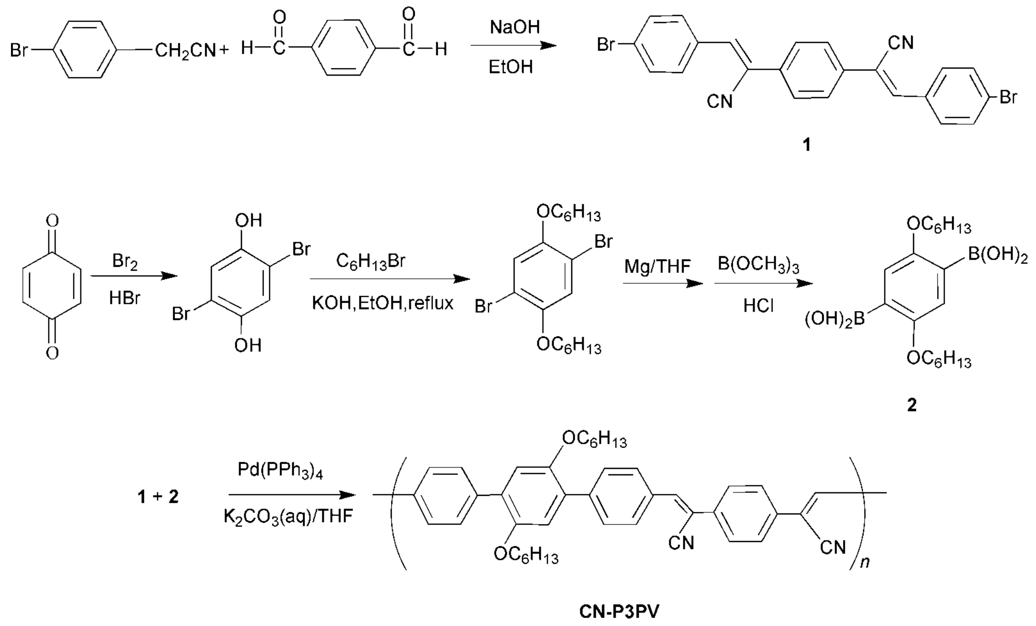
2,5-Dibromo-1,4-bis(hexyloxy)benzene was synthesized from 1,4-benzoquinone by a two-step reaction according to the literature method.[21] 2,5-Dibromo-1,4-bis(hexyloxy)benzene could be converted to 2,5-bis(hexyloxy)phenyl-1,4-diboronic acid monomer **2**, in 40–50% yield by reaction with magnesium to form a bifunctional Grignard reagent followed by treatment with trimethyl borate and acidic hydrolysis.[20–22]

The Suzuki coupling of monomer **1** with monomer **2** in the presence of $Pd(PPh_3)_4$ and K_2CO_3 (aq.) generated polymer CN-P3PV in 85% yield. CN-P3PV was purified by addition of its chloroform solution to methanol and precipitation three

DOI: 10.1039/b008521i

This journal is © The Royal Society of Chemistry 2001

Published on 22 March 2001. Downloaded by University of Michigan Library on 21/10/2014 20:56:10.



Scheme 1 Synthetic route of CV-P3PV *via* the Suzuki coupling reaction.

times. Some insoluble solid was also obtained, which may be the cross-linking by-products.

CN-P3PV is an orange powder and can be dissolved easily in conventional organic solvents such as methylene chloride, chloroform, toluene and tetrahydrofuran. The good solubility can be partially attributed to the two *n*-hexyloxy side-chains that are attached on the repeat units. The ^{1}H NMR spectrum of CN-P3PV was well resolved and indicated a well-defined polymer structure identical with the expected structure. Its molecular weight was revealed by gel permeation chromatography (GPC) using THF as eluent and polystyrene as the calibration standard. The weight-average (M_w) and the number-average (M_n) molecular weights of the polymer were 3000 and 1600 (PDI = 1.94), respectively. On the basis of the modestly low molecular weight, CN-P3PV is more strictly an oligomer than a polymer. From the information of elemental analysis, we can deduce that the Br atoms remain as the main terminal groups in the polymer. A pinhole free thin film was obtained readily by the spin-coating technique from its $CHCl_3$ solution.

The thermal properties of CN-P3PV were analyzed by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) under a nitrogen atmosphere. A typical TGA curve demonstrated a high thermal stability, up to 360 °C, with a heating rate of 20 °C min^{-1} (Fig. 1). DSC measurements revealed a glass transition temperature of 151 °C and no melting points were observed for the polymer before thermal decomposition. These results imply that the polymer is a good candidate as an EL material.

Electrochemical and photophysical properties of CN-P3PV

In order to gain information on the charge injection, electrochemical measurements were performed. Fig. 2 shows a full scan cyclic voltammogram (CV) for CN-P3PV. It exhibits irreversible waves under cathodic sweep and the main reaction took place at −1.55 V (onset potential), which was higher than its parent polymer, PPV (−1.99 V).[23a] The reduction process for a conjugated polymer in an electrochemical cell is related to the electron capture ability (or electron injection ability). Therefore it is reasonable to infer that the polymer CN-P3PV has a higher electron affinity than PPV, owing to the introduction of electron-withdrawing cyano groups. The oxidation exhibits an irreversible wave when swept anodically and the onset potential of oxidation for CN-P3PV is located at 0.82 V. This value is relatively high but lower than that for CN-PPV (1.0 V). Since the oxidation process for a conjugated polymer in an electrochemical cell is closely related to the removal of electrons (or the injection of the holes) from the HOMO of the material, a high oxidation potential of CN-P3PV (0.82 V) and an irreversible anodic wave present a barrier to hole injection. This may lead to an imbalance of charge

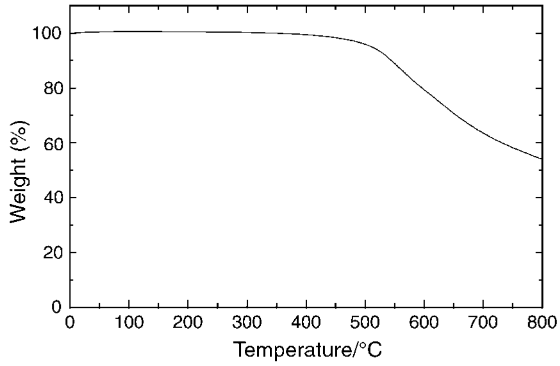


Fig. 1 Thermal gravimetric analysis (TGA) curve of CN-P3PV (under a nitrogen atmosphere at 20 °C).

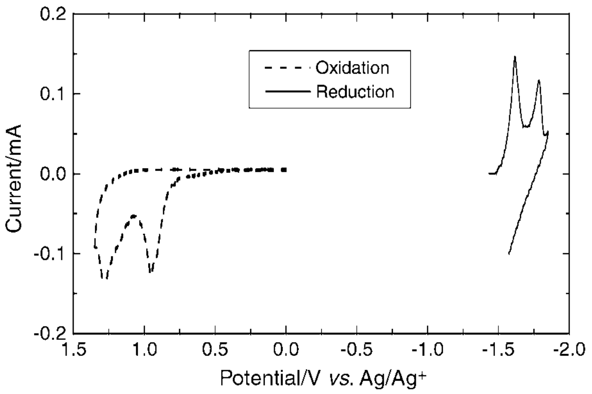


Fig. 2 Cyclic voltammogram of the CN-P3PV film spin-coated on ITO glass. (Measured in an acetonitrile solution of TBAP (0.1 M) at a scan rate of 40 mV s^{-1}, referenced *vs.* Ag/Ag$^+$ and calibrated externally *vs.* Fc/Fc$^+$ 0.12 V).

View Article Online

Published on 22 March 2001. Downloaded by University of Michigan Library on 21/10/2014 20:56:10.

Table 1 Electrochemical and optical parameters for polymer CN-P3PV[a]

	λ_{max}/ nm	E_g^{OPT}/ eV	E^{ox}/V	E^{red}/V	HOMO/eV	LUMO/eV
CN-P3PV	520	2.38	0.82	−1.55	−5.50	−3.13

[a] E_{FOC} = 0.12 V *vs.* Ag/Ag$^+$.

injection and charge transport for a single layer LED made by this polymer.

The redox potentials obtained from CV measurement for CN-P3PV are listed in Table 1. The HOMO and LUMO values were calculated by estimating the energy level of ferrocence (E_{FOC}) at −4.8 eV[23b] below the vacuum level. The formal potential of FOC was measured as 0.12 V against Ag/Ag$^+$. The low LUMO energy level (−3.13 eV) will greatly facilitate the electron injection from the cathode of the LED, indicating that an air stable metal, such as Al, can be used as a cathode. The band gap can be derived from the difference between the onset of the first oxidation potential and the first reduction potential (E_g^{EC} = 2.37 eV).

Fig. 3 shows the UV and photoluminescent (PL) spectra of CN-P3PV in $CHCl_3$ solution and as a thin solid film. In the absorption spectra of the polymer in $CHCl_3$ solution, the π–π* transition maximum and the edge of absorption appear at 414.5 nm and 520 nm, respectively. However, the absorption spectrum of the polymer film was red shifted by 20 nm compared with that of the polymer in solution. On the basis of the absorption band edge, the optical band gap of CN-P3PV is 2.38 eV (λ_{onset} = 520 nm, E_g^{OPT} = 2.38 eV). It is obvious that this value is in good agreement with the electrochemical value obtained from the CV data (E_g^{EC} = 2.37 eV). As compared to the CN-PPV measured by Holmes and co-workers,[18] the band gap for CN-P3PV is slightly larger (2.16–2.10 eV) due to the decrease of cyano-substituent content in the polymer chain. The polymer fluoresced orange under the irradiation of UV light and the emission maxima at 538 nm in $CHCl_3$ solution (excited at 365 nm) and 590 nm as a solid film (excited at 380 nm). As a film on a quartz substrate, the absorption bands and PL spectra became broad and shifted toward the longer wavelength region. This is due to the ground state energy increasing with increasing intermolecular interaction as a result of closer packing of the molecules in the film state. The fluorescence peak of the polymer was dramatically blue-shifted compared with that of CN-PPV (710 nm) owing to the decreased number of CN substituents and vinylene groups in CN-P3PV.

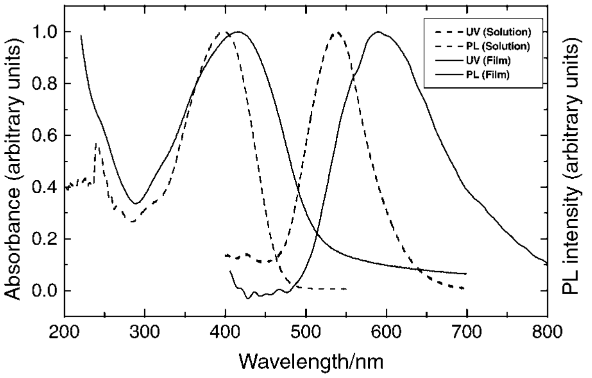


Fig. 3 UV-Vis and PL spectra for CN-P3PV in $CHCl_3$ solution (dashed line) and in solid film (solid line).

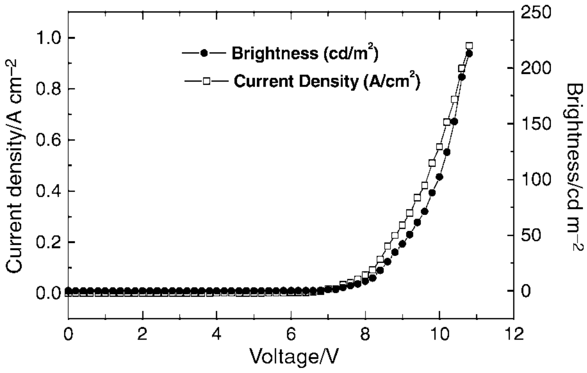


Fig. 4 *I–V–L* curve for the device of ITO/CuPc/CN-P3PV/Ca/Ag.

Electroluminescence properties

To investigate the EL properties of the polymer, a two-layer LED of ITO/CuPc/CN-P3PV/Ca/Ag was fabricated and studied, where CuPc was used as a hole-transporting layer. CN-P3PV may possess very good electron transporting properties and it needs the CuPc layer to balance the overall charge injection/transporting properties in order to optimize the performance of the multilayer LED. The typical current–voltage and light–voltage curves of this device are shown in Fig. 4. Bright orange light emission could be seen easily under normal light conditions. The current–voltage–brightness (*I–V–L*) characteristics of the device revealed an excellent diode behavior (Fig. 4), *i.e.*, under the forward bias, the current and the intensity of the emitting light increased superlinearly with the increase of applied voltage after surpassing the turn-on voltage (<7 V). Moreover, under reverse bias, no obvious increase of current was observed when the applied voltage was increased. The highest luminescence, before breaking the device, was 213 cd m^{-2} with an external quantum efficiency of 0.011% at 10.8 V and a current density of 9.7 mA mm^{-2}.

The electroluminescence spectra of the LED under different drive voltages and the photoluminescence spectra of a thin film of CN-P3PV are shown in Fig. 5. The PL spectra of CN-P3PV film have an emission peak at 590 nm and a shoulder emission at 555 nm when it was excited at 380 nm. The EL spectrum from the device was almost identical with the PL spectrum (film) of the polymer, indicating that the same excitation state was involved. At low drive voltage (6 V), a peak at 730 nm was noticeable, which could be observed from the PL spectrum. This emission is due to the formation of an excimer, a result of strong π electron repulsion as the separation distance is reduced between molecules. The EL intensity was increased with an increasing in applied voltages. Bright orange light emission was observed in daylight under forward bias for the LED, implying a high EL efficiency for the polymer. Considering that the device structure has not been optimized in this study, this result could be improved after the structural optimization.

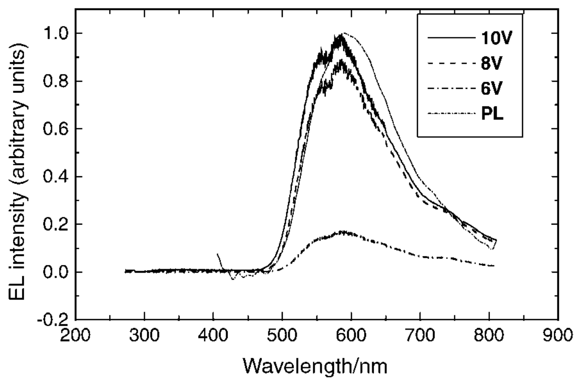


Fig. 5 Electroluminescent spectra of ITO/CuPc/CN-P3PV/Ca/Ag.

Published on 22 March 2001. Downloaded by University of Michigan Library on 21/10/2014 20:56:10.

Conclusion

In conclusion, a high performance light-emitting polymer containing the electron-affinity moiety of cyano group was synthesized *via* a Suzuki coupling reaction. This facile method provides the synthesis of light-emitting polymers with a broad variation of polymer backbones. The resulting polymer possesses high thermal stability, high electron affinity, good solubility and thin film forming properties. In addition, we have shown the EL properties of the PPV derivative in organic LEDs, and bright orange light emission was achieved for the LED fabricated with this polymer. From these results we believe that CN-P3PV is a new candidate for a light emitting material in organic LEDs.

Experimental

Materials

All the solvents used in this study were purified according to standard methods prior to use, and all other chemicals were of reagent grade and were used as purchased without further purification. 2,5-Dibromohydroquinone, 2,5-dibromo-1,4-bis(hexyloxy)benzene, and monomer **2** were synthesized by reactions according to the literature.[20–22] The catalyst tetrakis(triphenylphosphine)palladium(0) was synthesized by a literature method.[24]

Synthesis

1,4-Bis(β-cyano-*p*-bromostyryl)benzene (1). 4-Bromophenylacetonitrile (1.96 g, 10 mmol) and terephthalaldehyde (0.62 g, 5 mmol) were dissolved in 50 mL of dry ethanol under a nitrogen atmosphere in 100 mL three-necked round-bottomed flask. A mixture of 50 mg of sodium hydroxide and 30 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 out and washed with water. A yellow powder was obtained.

^{1}H NMR (200 MHz, d$_6$-DMSO, ppm): δ 8.1 (2H, s, vinyl H), 8.0 (2H, d, arom. H), 7.6–7.8 (8H, m, arom. H), 7.3 (2H, d, arom. H). Anal. Calcd. for $C_{24}H_{14}N_2Br_2$: C, 58.81; H, 2.88; N, 5.71. Found: C, 58.45; H, 3.18; N, 5.51%.

Polymer. Under N_2, a mixture of **1** (0.490 g, 1 mmol), **2** (0.366 g, 1 mmol) and $Pd(PPh_3)_4$ (53 mg, 0.05 mmol) in THF (7.5 mL) and K_2CO_3 (7.5 mL, 1 M aqueous solution) was refluxed for 48 h. $CHCl_3$ (100 mL) was added to this reaction mixture, and the organic layer was separated. The solution was washed with brine and dried over Na_2SO_4. The solution was concentrated under vacuum, methanol was added to precipitate out the polymer. The precipitation process was repeated 3 times. After drying under vacuum, a bright orange powder was obtained.

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 0.90 (6H, m, CH_3), 1.31–1.44 (12H, m, CH_2), 1.73–1.88 (4H, m, CH_2), 3.99 (4H, m, OCH_2), 7.05 (2H, m, arom. H), 7.81–7.56 (12H, m, arom. H), 8.05 (4H, m, arom. H and vinyl H). FT-IR (KBr, cm^{-1}): 3033.24 (w), 2955.26 (s), 2929.99 (s), 2858.89 (s), 2214.40 (m), 1605.08 (m), 1523.37 (w), 1492.10 (s), 1468.72 (s), 1423.35 (w), 1386.33 (s), 1261.55 (s), 1209.40 (s), 1053.23 (s), 1017.72 (s), 943.5 (w), 905.21 (w), 835.03 (s), 803.40 (s), 726.82 (w). Anal. Found for CN-P3PV: $[(C_{42}H_{42}N_2O_2)_nBr_2$, $n=3$–5]: C, 77.53; H, 6.79; N, 3.97; Br, 5.90%.

Measurement

FT-IR spectra were taken on a Perkin-Elmer SYSTEM 2000 FT-IR spectrometer with KBr pellets. UV-Vis spectra were recorded on a Perkin-Elmer Lambda-9 UV-Vis near infrared spectrophotometer. ^{1}H NMR spectral data are expressed in ppm relative to internal standard tetramethylsilane and were obtained on a Bruker dmx (300 NMR) and Varian (200 NMR) spectrometers. Elemental analysis were taken on a Carlo Erba 1106 elemental analyzer, and bromine atom was analyzed by mercurimetric determination

TGA and DSC measurements were performed on a Perkin-Elmer Series 7 thermal analysis system under N_2 at a heating rate of 20 °C min^{-1}. The weight average molecular weight (M_w) and polydispersity index of polymer were measured on PL-GPC Model 210 chromatograph at 35 °C, using THF as eluent and standard polystyrene as reference. Electrochemical measurements were performed on a voltammetric analyzer using cyclic voltammetry at room temperature in a conventional three-electrode cell with a polymer thin film spin-coating onto indium tin oxide (ITO) glass as the working electrode (3 cm^2). Pt gauze was used as the counter electrode and Ag/Ag$^+$ was used as the reference electrode, with 0.1 M tetrabutylammonium perchlorate (TBAP) in acetonitrile as the electrolyte.

The EL device was constructed using a double-layer structure with copper phthalocyanine as the hole transporting layer and CN-P3PV as the emitting layer. Prior to the deposition of these organic films, the ITO-coated glass substrate was cleaned by sequential ultrasonic washing in detergent solution, deionized water, methanol, and chloroform for 30 min, respectively, and finally rinsed with acetone for 2 h in a Soxhlet extractor. CuPc, Ca and Ag layers were evaporated under vacuum. A thin film of CN-P3PV was spin-coated from $CHCl_3$ solution at 2000 rpm for 20 s. The thicknesses of CuPc and CN-P3PV were 50 nm, and the active area of the resulting device was 0.07 cm^2. All device testing was carried out at room temperature under an ambient atmosphere. Photometric units (cd m^{-2}) were calculated using the forward output power and the EL spectra of the devices, assuming Lambertian distribution of the EL emission.[25]

Acknowledgements

The author would like to thank the National Natural Science Foundation of China, a Key Program of Chinese Academy of Sciences.

References

1 J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burn and A. B. Holmes, *Nature*, 1990, **347**, 539.

2 (*a*) G. Grem, G. Leditzky, B. Ullrich and G. Leising, *Adv. Mater.*, 1992, **4**, 36; (*b*) M. Remmers, D. Neher, J. Grüner, R. H. Friend, G. H. Gelinck, J. M. Warman, C. Quattrocchi, D. A. dos Santos and J-L. Brédas, *Macromolecules*, 1996, **29**, 7432.

3 (*a*) P. L. Burn, A. B. Holmes, A. J. Kraft, D. D. C. Bradley, R. H. Friend and A. R. Brown, *J. Chem. Soc., Chem. Commun.*, 1992, 32; (*b*) D. H. Hwang, H-K. Shom, J-I. Lee and K-S. Lee, *J. Chem. Soc.,Chem. Commun.*, 1994, 2461.

4 N. C. Greenham, S. C. Moratti, D. D. C. Bradley, R. H. Friend and A. B. Holmes, *Nature*, 1993, **365**, 628.

5 Y. Q. Liu, X. Z. Jiang, Q. L. Li and D. B. Zhu, *Synth. Met.*, 1997, **4**, 36.

6 Z. Peng, Z. Bao and M. E. Galving, *Adv. Mater.*, 1998, **10**(9), 680.

7 Y. Q. Liu, M. S. Liu, X. C. Li and A. K.-Y. Jen, *Chem. Mater.*, 1998, **10**, 3301.

8 X.-C. Li, Y. Q. Liu, M. S. Liu and A. K.-Y. Jen, *Chem. Mater.*, 1999, **11**, 1568.

9 J. R. Sheats, M. Antoniadis, M. Hueschen, W. Leonard, J. Miller, R. Moon, D. Roitman and A. Stocking, *Science*, 1996, **273**, 884.

10 I. D. Parker, *J. Appl. Phys.*, 1994, **75**, 1656.

11 M. Onoda, *J. Appl. Phys.*, 1995, **78**, 1327.

12 D. Braun and A. J. Heeger, *Appl. Phys. Lett.*, 1991, **58**, 1982.

13 C. W. Tang and S. A. Vanslyke, *Appl. Phys. Lett.*, 1990, **57**, 913.

14 C. Adachi, T. Tsutsui and S. Saito, *Appl. Phys. Lett.*, 1990, **57**, 531.

Published on 22 March 2001. Downloaded by University of Michigan Library on 21/10/2014 20:56:10.

15 H. V. Zhang, B. Seggern, H. W. Krabel, H. Schmidt and A. J. Heeger, *Synth. Met.*, 1995, **72**, 185.
16 (*a*) Y. Q. Liu, H. Ma, M. S. Liu, S. Liu and A. K.-Y. Jen, *Proc. SPIE – Int. Soc. Opt. Eng.*, 1999, **3623**, 28; (*b*) Y. Q. Liu, H. Ma and A. K.-Y. Jen, *Chem. Commun.*, 1998, 2747.
17 J. H. Segura and N. Martin, *J. Mater. Chem.*, 2000, **10**, 2403.
18 (*a*) N. C. Greenham, S. C. Moratti, D. D. C. Bradley, R. H. Friend, P. L. Burn and A. B. Holmes, *Nature*, 1993, **365**, 628; (*b*) A. C. Grimsdale, F. Cacialli, J. Gruner, X. C. Li, A. B. Holmes, S. C. Moratti and R. H. Friend, *Synth. Met.*, 1996, **76**, 165.
19 U. Mitschke and P. Bäuerle, *J. Mater. Chem.*, 2000, **10**, 1471.
20 I. G. C. Count, H. R. Goldschmid and O. C. Musgrave, *J. Chem. Soc. C*, 1970, 488.
21 V. Thomas and W. Gerhard, *Macromol. Chem. Phys.*, 1994, **195**, 1933.
22 R. N. Donald and E. M. William, *J. Am. Chem. Soc.*, 1957, **79**, 3081.
23 (*a*) Y. Q. Liu, M. S. Liu and A. K.-Y. Jen, *Acta Polym.*, 1999, **50**, 105; (*b*) J. Pommerehne, H. Vestweber, W. Guss, R. F. Mahrt, H. Bässler, M. Porsch and J. Daub, *Adv. Mater.*, 1995, **7**, 551.
24 D. R. Coulson, *Inorg. Synth.*, 1972, **13**, 121.
25 N. C. Greenham, R. H. Friend and D. D. C. Bradle, *Adv. Mater.*, 1994, **6**, 491.