Polymers with High Electron Affinities for Light-Emitting Diodes

Zhonghua Peng and Mary E. Galvin*

Bell Laboratories, Lucent Technologies 600 Mountain Avenue Murray Hill, New Jersey 07974

Polymers with high electron affinities have been widely used as electron injection/transport layers in polymer light-emitting diodes. Among them, cyano-containing poly(phenylenevinylene)s (CN−PPVs) have been demonstrated to be highly efficient in electron transport. These CN−PPVs are synthesized by a Knoevenagel-type condensation between an aromatic diacetonitrile and a corresponding aromatic dialdehyde. Careful control of reaction conditions is required to avoid side reactions and the polymer molecular weight is usually low. In this paper, we report a CN−PPV synthesized by the Heck coupling reaction. We also report a new pyrazine-containing PPV. Both polymers show good electron injection/transport ability and luminescence properties. Single layer LED devices with the configuration of (ITO/polymer/Al) show external quantum efficiencies up to 0.025%.

Introduction

Polymeric light emitting diodes (LEDs) have been extensively studied recently due to their promise for practical applications.[1−8] A wide range of polymers as well as polymer blends have been used as emissive materials.[9−12] Light emission is produced in the luminescent polymer layer via recombination of electrons and holes injected from the two electrodes. It is known that balanced charge injection from both electrodes and comparable mobility of both charge carrier types inside the polymer are crucial for high device efficiencies.[13,14]

The facility of charge injection depends on the barriers between the molecular frontier orbitals of the polymer (HOMO for hole injection and LUMO for electron injection) and the work function of the contact metal electrodes. In general, polymer LEDs have smaller hole injection barriers than electron injection barriers. Although electron injection can be facilitated by using low work function metals such as calcium or magnesium as cathodes,[15,16] the instability of such metals toward air and moisture limits their practical applications. Another more practical approach is to lower the LUMO of the polymer by increasing the electron affinity of the polymer. Such an approach has been shown to be very successful.[17,18] Polymers with cyano-substituents in the backbone have been used as an electron-transporting layer in a two-layer LED in which PPV was the hole-transporting layer. These devices had an internal quantum efficiency of 4%.[18]

We have been pursuing efficient single-layer LED devices.[19,20] In this paper, we report a new pyrazine-containing PPV which is as efficient in electron transport as CN−PPVs. Distyrylpyrazines have been reported to possess both high electron affinity and efficient fluorescence.[21,22] However, no polymer containing pyrazine in the conjugated chain has been reported and tested for LED devices. We also report a CN-containing PPV which was synthesized by the Heck coupling reaction. CN−PPVs reported so far are synthesized by the Knoevenagel-type condensation.[17,18] The latter requires a significant amount of alcohol (methanol or

* Current address of corresponding author: Department of Materials Science, University of Delaware, Newark, DE 19716

(1) 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.

(2) Kido, J. *Trends Polym. Sci.* **1994**, *2*, 350.

(3) Dodabalapur, A. *Solid State Commun.*, **1997**, *102*, 259−267.

(4) Bradley, D. D. C. *Synth. Met.* **1993**, *54*, 401.

(5) Zhang, C.; Hoger, S.; Pakbaz, K.; Wudl, F.; Heeger, A. J. *J. Electron. Mater.* **1994**, *23*, 453.

(6) Lögdlund, M.; Dannetun, P.; Stafström, S.; Salaneck, W. R.; Ramsey, M. G.; Spangler, C. W.; Fredriksson, C.; Brédas, J.-L. *Phys. Rev. Lett.* **1993**, *70*, 970.

(7) Tarkka, R. M.; Zhang, X.; Jenekhe, S. *J. Am. Chem. Soc.* **1996**, *118*, 9438.

(8) Berggren, M.; Inganäs, O.; Rasmusson, J.; Gustafsson, G.; Andersson, M. R.; WennerstrÖm, O.; Hjertberg, T. *Nature*, **1994**, *372*, 444.

(9) Yamamota, T.; Suganuma, H.; Maruyama, T.; Inoue, T.; Muramatsu, Y.; Arai, M.; Komarudin, D.; Ooba, N.; Tomaru, S.; Sasaki, S.; Kubota, K. *Chem. Mater.* **1997**, *9*, 1217.

(10) Blatchford, J. W.; Jessen, S. W.; Lin, L. B.; Gustafson, T. L.; Epstein, A. J.; Fu, D. K.; Wang, H. L.; Swager, T. M.; Macdiarmid, A. G. *Phys. Rev. B* **1996**, *54*, 9180.

(11) Wu, C. C.; Sturm, J. C.; Register, R. A.; Tian, J.; Dana, E. P.; Thompson, M. E. *IEEE Transactions on Electron Devices* **1997**, *44* (8), 1269.

(12) Politis, J. K.; Nanos, J.; He, Y.; Kanicki, J.; Curtis, M. D. *Proc. Mater. Res. Soc. Symp.* **1997**, *424*, 495.

(13) Brown, A. R.; Bradley, D. D. C.; Burn, P. L.; Burroughes, J. H.; Friend, R. H.; Greenham, N.; Kraft, A. *Appl. Phys. Lett.* **1992**, *61*, 2793.

(14) Parker, I. D.; Pei, Q.; Marrocco, M. *Appl. Phys. Lett.* **1994**, *65*, 1272.

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

(16) Gustafsson, G.; Cao, Y.; Treacy, G. M.; Klavetter, F.;. Colaneri, N.; Heeger, A. J. *Nature* **1992**, *357*, 477.

(17) Moratti, S. C.; Cervini, R.; Holmes, A. B.; Baigent, D. R.; Friend, R. H.; Greenham, N. C.; Grüner, J.; Hamer, P. J. *Synth. Met.* **1995**, *71*, 2117.

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

(19) Peng, Z. H.; Bao, Z.; Galvin, M. E. *Adv. Mater.* Submitted.

(20) Peng, Z. H.; Bao, Z.; Galvin, M. E. *Chem. Mater.* Submitted.

(21) Grimsdale, A. C.; Cervini, R.; Friend, R. H.; Holmes, A. B.; Kim, S. T.; Moratti, S. C. *Synth. Met.* **1997**, *85*, 1257.

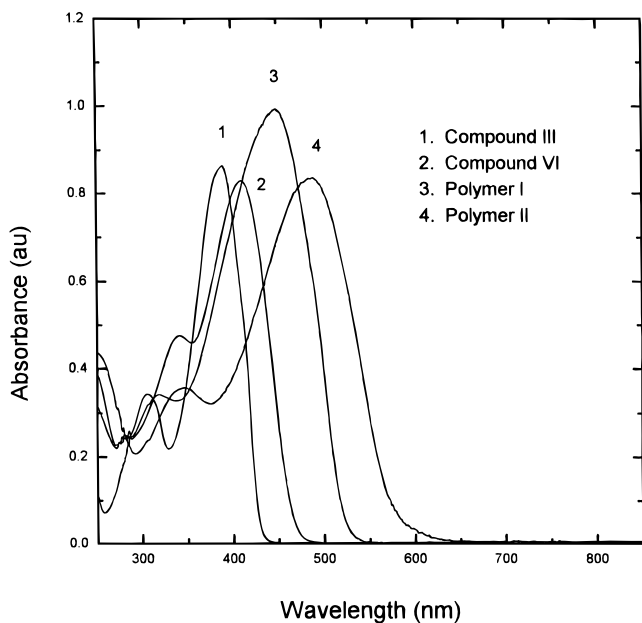(22) Nohara, M.; Hasegawa, M.; Hosokawa, C.; Tokailin, H.; Kusumoto, T. *Chem. Lett.* **1990**, 189.

Figure 1. UV/vis spectra of the monomers and the polymers.
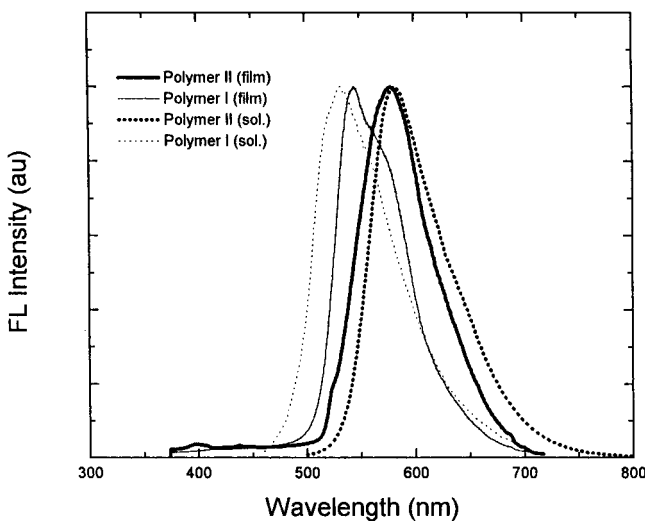

Figure 2. The fluorescence spectra of the polymers in solution and as solid films.

butanol), typically poor solvents for polymers as the reaction medium, and careful control of reaction conditions. The molecular weights of the resulting polymers are usually low. By Heck coupling, better control of the polymerization and polymers with higher molecular weights can be achieved.[23]

Results and Discussion

The structures of the polymers are shown in Scheme 1. Both polymer backbones are substituted PPVs. In polymer **I**, there is one pyrazine ring for every three phenyl rings. Polymer **II** has two cyano substituents for every four phenyl rings. The number of CN substituents is half of that of the CN−PPV reported by the Cambridge group.[18]

The synthesis of the polymers is shown in Scheme 2. Zinc chloride catalyzed condensation of 2,5-dimeth-

Scheme 1. the Structures of the Polymers

Polymer **I**
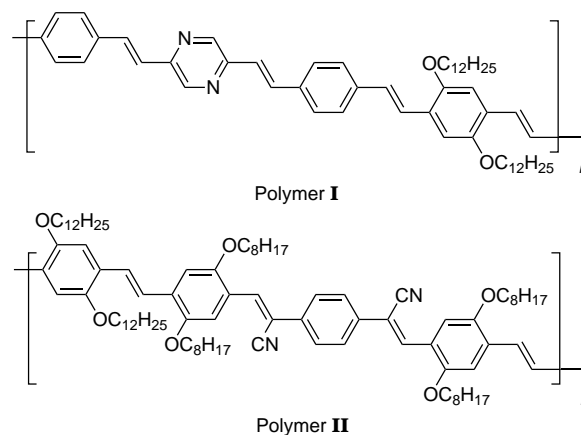
Polymer **II**

ylpyrazine with 4-bromobenzaldehyde gave compound **III** in over 70% purified yield.[24] Polymerization of compound **III** with dialkoxydivinyl benzene[20] (**IV**) by Heck coupling in DMF yielded red polymer **I**. For polymer **II**, Knoevenagel type condensation of benzyl-diacetonitrile with compound **V** gave compound **VI** in 71% yield. Subsequent polymerization under Heck coupling conditions gave polymer **II** as a dark red powder in over 90% yield. Both polymers were purified by redissolving in THF and reprecipitation into methanol. Polymers **I** and **II** have number average molecular weights of 12 and 18 kDa, respectively, as measured by gel permeation chromotography using polystyrene standards. The actual molecular weight of polymer **I** may be smaller on the basis of elemental analysis and end group analysis.[25] Both polymers are soluble in common organic solvents such as chloroform, THF, and tetrachloroethane.

The UV/vis spectra of the polymers are shown in Figure 1. For comparison, the spectra of compounds **III** and **VI** are also shown in the graph. The $\pi-\pi^*$ transition maximum and edge of polymer **I** appeared at 448 and 525 nm, respectively. For polymer **II**, these transitions appear at much longer wavelengths of 490 and 575 nm. On the basis of the absorption band edges, the band gap energies of polymers **I** and **II** are 2.37 and 2.16 eV, respectively. As compared to the Cambridge CN−PPV, the band gap of polymer **II** is slightly larger (2.16−2.1 eV) due to the lower cyano-substituent content of the polymer chain.

Both polymers are strongly fluorescent. The photoluminescence spectra of both polymers in THF solution and as solid films are shown in Figure 2. Polymer **I** has an emission maximum at 530 nm in THF solution (excited at 450 nm) and 550 nm as a solid film (excited at 441.6 nm). Polymer **II**, however, whether in solution

(23) Brenda, M.; Greiner, A.; Heitz, W. *Makromol. Chem.* **1990**, *191*, 1083.

(24) Yamada, S.; Ueda, T. Jpn. Patent 1961, 3367.

(25) The proton NMR of polymer **I** shows small but clear signals from protons at the end vinyl groups. The ratio of the end vinyl protons (germinal protons) versus alkoxy −OCH₂− protons was found to be 1:16 on the basis of the integration of the spectra. If we assume only one end of the polymer chain is vinyl group (the other end would be bromine), the above end group analysis would imply a polymer with an average repeating unit of 8, which corresponds to a number average molecular weight of 6300. The polymer would have an average repeating unit of 16 if both polymer chain ends are vinyl groups. However, elemental analysis showed a significant amount of bromine in the polymer (1.07%). Again, if we assume one polymer chain end is bromine, the polymer would have a molecular weight of 7500 (calculated by 79.9/0.0107) based on the bromine content inside the polymer.

Scheme 2. Synthesis of the Polymers

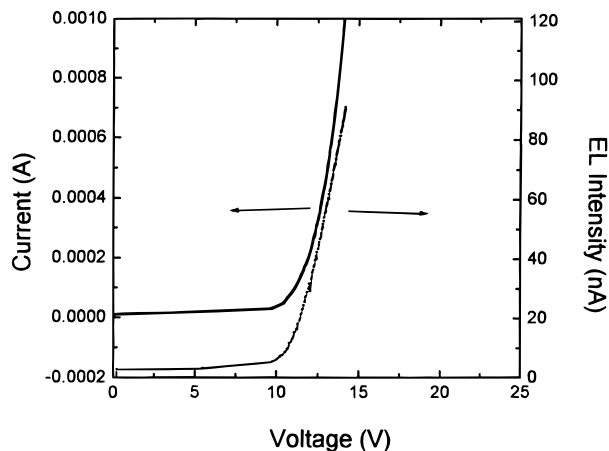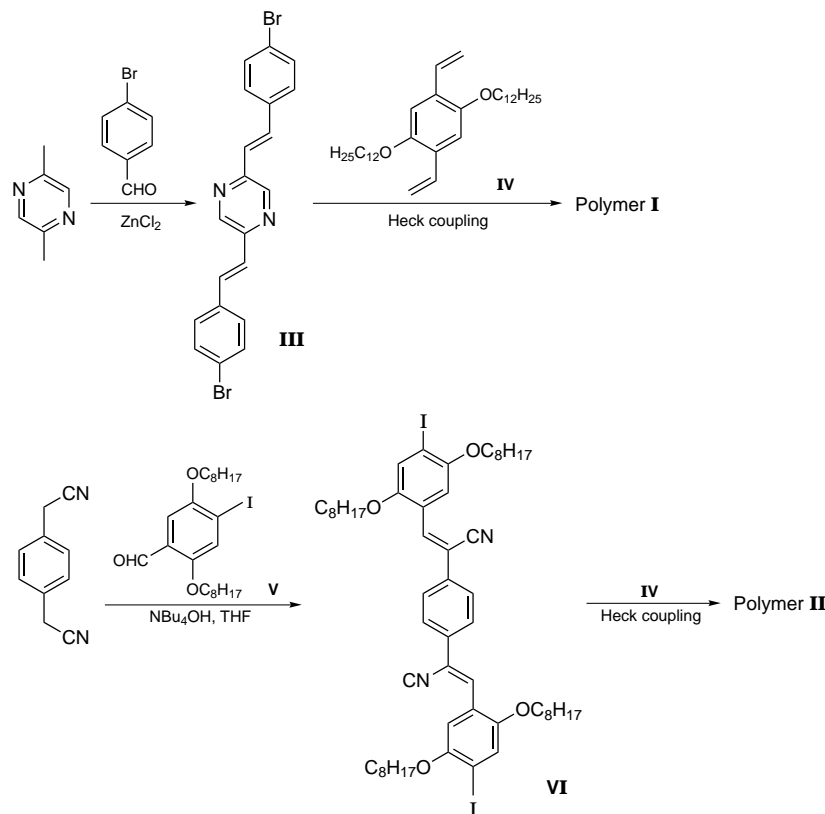**Figure 3.** Light−current−voltage characteristics of an (ITO/polymer I/Al) device.

Figure 4. Light−current−voltage characteristics of an (ITO/polymer II/Al) device.

(excited at 490 nm) or as a film (excited at 441.6 nm), has a very similar emission maximum at 590 nm. The fluorescence peak at 590 nm is dramatically blue-shifted compared to the 710 nm of the Cambridge CN−PPV. It is rather surprising that decreasing the CN content in the polymer's main chain, which causes only a slight blue shift in the absorption, causes such a dramatic shift in the luminescence of the polymer. This result could imply less interchain interactions among our CN−PPVs.

Single-layer LED devices using polymer **I** or **II** as the emissive medium were fabricated. Thin films were spin-coated from tetrachloroethane solution onto glass substrates coated with indium tin oxide. A layer of aluminum (1000∼2000 Å) was then deposited by vacuum evaporation. Current−light−voltage characteristics of the devices were measured using a HP4155A Semiconductor Parameter Analyzer with a calibrated silicon
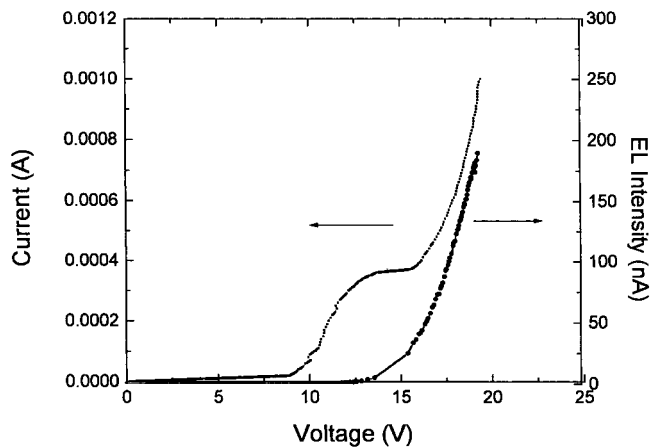
photodiode detector. External quantum efficiencies were calculated as the ratio of photocurrent over electric current with a modification factor of 1.32 (correction factor of the detector sensitivity).

Devices based on both polymers showed uniform orange emission. The typical current−light−voltage curves for both polymer devices are shown in Figures 3 and 4. The light intensity was shown as photodiode current in the figures (1 nA = 1.32 nW). Polymer **I** has a turn-on voltage of 10 V for both the light and the current, indicating a reasonably balanced charge injection. The external quantum efficiency was calculated to be 0.012% at a current density of 1 mA/mm². LED devices based on polymer **II** have a higher efficiency of 0.025%. When calcium was used as the metal electrode, devices based on both polymers **I** and **II** show no obvious improvement in the efficiencies. These results suggest

that the electron injection in both polymers **I** and **II** is significantly improved as compared to alkoxy-substituted PPV derivatives.[19,20] For polymer **II**, however, the electron injection is so facilitated that the hole injection and transport becomes the limiting factor. As shown in Figure 4, while the current turns on at 9 V, the light does not turn on until 14 V, indicative of an imbalance in the injection of opposite charges. The bump shape of the current−voltage curve is very reproducible. We believe the electrons can be injected at lower voltages than that of the holes. To verify such an assessment, bilayer devices with a configuration of (ITO/PPV/polymer **I** or **II**/Al) were also fabricated. The PPV layer was thermally converted from its xanthate precursor as reported previously.[26] Bilayer devices based on polymer **II** have an efficiency of 0.062%, 3 times higher than its single-layer devices. Bilayer devices based on polymer **I** show only a slightly higher efficiency of 0.015%. It is worth mentioning that our device fabrication (except cathode evaporation) and demonstration are all performed in air without taking precautions. Efficiency calculations are based solely on the photocurrent detected and electric current measured, no corrections regarding light losses through mechanisms such as reflection, absorption, or waveguiding were made. Higher efficiency LED devices might be fabricated with optimized conditions.

Conclusion

We have synthesized two novel polymers, a pyrazine-containing PPV and a cyano-containing PPV, by the Heck coupling reaction. Both polymers showed good LED performance in a single-layer configuration of ITO/polymer/Al. The CN−PPV appears to be a better electron transporter than hole transporter, indicating that further work on two-layer devices is warranted.

Experimental Section

Compound III. A mixture of 2,5-dimethylpyrazine (2.00 g, 0.02 mol), 4-bromobenzaldehyde (20.00 g, 0.11 mol), and $ZnCl_2$ (2.00 g, 0.01 mol) was stirred at 170 °C for 12 h and was then poured into methanol. The brown precipitate was collected by filtration and recrystallized from THF to give compound **III** as shiny yellow crystals (5.10 g, 62%, mp: 276−277 °C). ^1H NMR (CDCl$_3$, ppm): δ 7.13 (d, J = 16.20 Hz, 2H, vinyl protons), 7.42 (d, J = 8.03 Hz, 2H, aromatic protons), 7.48 (d, J = 8.00 Hz, 2H, aromatic protons), 7.64 (d, J = 16.13 Hz, 2H, vinyl protons), 8.54 (s, 2H, aromatic protons). Anal. Calcd for $C_{20}H_{14}N_2Br_2$: C, 54.33; H, 3.19; N, 6.33. Found: C, 54.25; H, 3.16; N, 6.27.

Compound IV. A solution of 2,5-didodecoxyl-1,4-diiodobenzene (5.52 g, 7.88 mmol), vinyltributyltin (5.00 g, 15.77 mmol), Pd(PPh$_3$)$_4$ (0.36 g, 0.30 mmol), and DMF (30.00 mL) was stirred at 100 °C for 5 h. After filtration, the filtrate was poured into water and extracted with methylene chloride. The organic layer was collected and dried over MgSO$_4$. The solvent was then removed and the residue was purified by running it through a short column with hexane:ethyl acetate = 30:1 as eluent. The product was a white powder (2.38 g, 59%, mp: 62−63 °C). ^1H NMR (CDCl$_3$, ppm): δ 0.88 (t, J = 6.72 Hz, 6H, CH$_3$), 1.26 (m, 32H, alkyl protons), 1.47 (m, 4H, alkyl protons), 1.79 (m, 4H, alkyl protons), 3.95 (t, J = 6.46 Hz, 4H, −OCH$_2$−), 5.24 (d, J = 11.23 Hz, 2H, vinyl protons), 5.72 (d, J = 16.74 Hz, 2H, vinyl protons), 6.98 (s, 2H, aromatic protons), 7.02 (dd, J = 6.62 Hz and 11.17 Hz, 2H, vinyl protons). Anal. Calcd for $C_{34}H_{58}O_2$: C, 81.86; H, 11.72. Found: C, 81.58; H, 11.57.

Compound VI. Tetrabutylammonium hydroxide (0.15 mL of a 1.0 M solution in methanol, 0.15 mmol) was added dropwise into a solution of 2,5-dioctoxyl-4-iodobenzaldehyde (1.50 g, 3.07 mmol), 1,4-phenylenediacetonitrile (0.24 g, 1.53 mmol), THF (6 mL), and butanol (6 mL) at 50 °C. The resulting solution was stirred at 50 °C for another 0.5 h and was then poured into methanol. The red crude product was collected by filtration and recrystallized from THF/methanol to give 1.20 g of product (71%, mp: 114−115 °C). ^1H NMR (CDCl$_3$, ppm): δ 0.89 (m, 12H, CH$_3$), 1.30−1.37 (m, 32H, alkyl protons), 1.51 (m, 8H, alkyl protons), 1.85 (m, 8H, alkyl protons), 3.98 (t, J = 6.53 Hz, 4H, −OCH$_2$−), 4.08 (t, J = 6.33 Hz, 4H, −OCH$_2$−), 7.37 (s, 2H, vinyl protons), 7.73 (s, 2H, aromatic protons), 7.75 (s, 4H, aromatic protons), 7.99 (s, 2H, aromatic protons). Anal. Calcd for $C_{56}H_{78}O_4N_2I_2$: C, 61.31; H, 7.17; N, 2.55. Found: C, 61.50; H, 6.91; N, 2.66.

Polymer I. A mixture of compound **III** (0.3000 g, 0.6785 mmol), compound **IV** (0.3384 g, 0.6785 mmol), Pd(OAc)$_2$ (0.0060 g, 0.0271 mmol), tri-*o*-tolylphosphine (0.0410 g, 0.1350 mmol), triethylamine (0.25 mL), and DMF (10 mL) was stirred at 80 °C for 5 h. The hot solution was poured into methanol and the polymer precipitated as a reddish-brown solid. The polymer was collected by filtration. To purify the polymer, it was redissolved in hot THF. After filtration, the filtrate was poured into methanol. The polymer was collected by filtration and dried under vacuum at 50 °C overnight (0.43 g, 81% yield). ^1H NMR (CDCl$_3$, ppm): δ 0.87 (b, 6H, CH$_3$), 1.26 (b, 32H, alkyl protons), 1.53 (b, 4H, alkyl protons), 1.85 (b, 4H, alkyl protons), 4.00 (b, 4H, −OCH$_2$), 7.12 (b, 8H, vinyl protons), 7.48 (b, 10H, aromatic protons), 8.56 (b, 2H, aromatic protons). Anal. Calcd for $C_{54}H_{70}O_2N_2$: C, 83.24; H, 9.06; N, 3.59. Found: C, 80.37; H, 7.92; N, 3.43.

Polymer II. Similar conditions were used as in the synthesis of polymer **I**. Polymer **II** was obtained as a dark red powder (93% yield). ^1H NMR (CDCl$_3$, ppm): δ 0.86 (b, 18H, CH$_3$), 1.18−1.57 (m, 76H, alkyl protons), 1.86 (b, 12H, alkyl protons), 3.86−4.13 (m, 12H, OCH$_2$), 7.18 (b, 2H), 7.55 (b, 2H), 7.75−7.81 (m, 8H), 7.93 (b, 2H), 8.11 (b, 2H). Anal. Calcd for $C_{90}H_{134}O_6N_2$: C, 80.67; H, 10.08; N, 2.09. Found: C, 79.55; H, 9.75; N, 2.11.

CM970697W

(26) Son, S.; Dodabalapur, A.; Lovinger, A. J.; Galvin, M. E. *Science* **1995**, *269*, 376.