Polymers with Bipolar Carrier Transport Abilities for Light Emitting Diodes

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Efficient and stable polymer light emitting diodes (LEDs) have recently been extensively pursued. To achieve efficient LED performance for a single layer device, a polymer with bipolar carrier transport abilities and high-luminescence quantum yields is desired. We envision that if an emissive polymer combines both electron and hole transporting segments, it could possess comparable bipolar carrier transport ability. In this paper, we report two oxadiazole-containing poly(phenylenevinylenes) (PPVs). An oxadiazole unit is introduced into the polymer backbone to improve the electron injection/transport properties. The oligo-(phenylenevinylene) segments function as both hole transporter and emitter. In one polymer, carbazole is introduced in the side chain to improve the hole tranport properties. The syntheses and device evaluations of these polymers are reported.

Introduction

Ever since the first report of polymer light emitting diodes in 1990,[1] tremendous progress has been made in terms of both device operation efficiency and lifetime.[2−8] Polymer light emitting diodes (LEDs) emitting light from blue to red with external quantum efficiencies over 1% have been developed.[2−8] The excitement of polymer LEDs comes from the fact that they are easier to fabricate than devices made from evaporated organic materials. The intrinsic film forming abilities of polymers cast from solution by convenient wet coating techniques are an attractive advantage for practical applications.[9−12]

Light emitted from polymer LEDs is produced via the recombination of electrons and holes injected through the electrodes. It is known that balanced and efficient charge injection/transport for both carrier types (electron and hole) is essential for high device efficiency. Polymers, however, are rarely good conductors for both electrons and holes. In most cases, they transport holes better than electrons. To facilitate the charge injection/transport, two approaches have been applied. One is to apply an additional electron injection/transport layer

between the emitter and cathode or/and a hole transporting layer between the emitter and the anode.[8,13−15] Such an approach has been very successful in improving device efficiency and stability. As a matter of fact, the most advanced polymer LEDs are based on such multilayer devices. However, the fabrication of multilayer polymer LEDs is usually difficult. From a cost-effective point of view, single layer polymer LEDs are preferred. To make a single layer device with bipolar transporting properties, polymer blends which contain a polymer matrix doped with necessary components, usually small molecules to facilitate electron/hole transporting properties, have been used.[16−18] This approach has been attractive due to ease of device fabrication and color tuning, as well as improved performance. A major concern is device stability. With dopants normally over 40%, phase separation is unavoidable at even ambient conditions, let alone the high current density and local heating that can occur during device operations. A logical approach for solving this problem is to synthesize a polymer containing both electron and hole transporting segments as well as emissive units.[19]

Polymers containing oxadiazole derivatives either in the main chain or side chains have been widely used as electron transporting/hole blocking materials in organic LEDs.[20−24] We have recently shown[25] that, by introduc-

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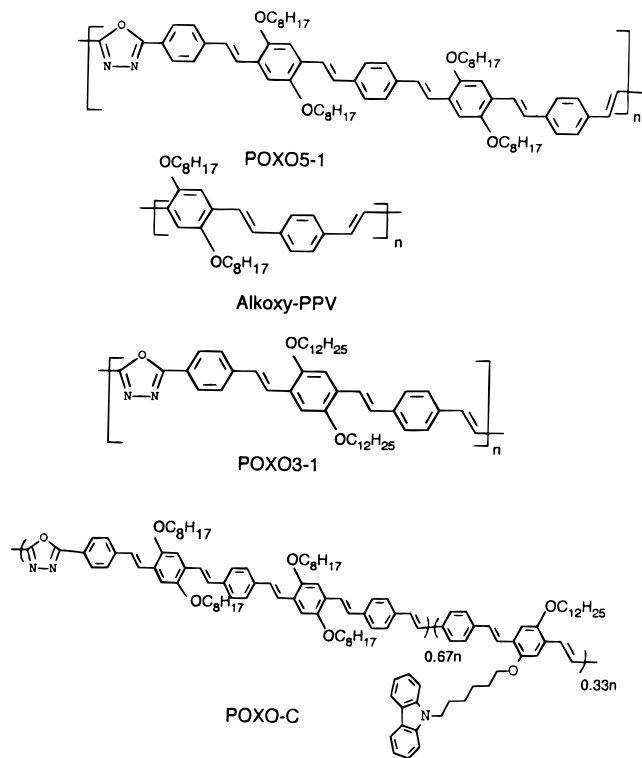(17) Johnson, G. E.; Mcgrane, K. M.; Stolka, M. *Pure Appl. Chem.* **1995**, *67*, 175.
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Chart 1. Structures of the Polymers

POXO5-1

Alkoxy-PPV

POXO3-1

POXO-C

ing oxadiazole moieties into a poly(phenylenevinylene) (PPV) backbone (POXO5-1, Chart 1), the electron injection/transporting properties of the resulting polymer are dramatically improved, in comparison with the corresponding PPV (alkoxy-PPV, Chart 1). Single layer LEDs with aluminum as the cathode showed external quantum efficiencies up to 0.15% and good device stability. To explore the possibility of further improving the device performance, we synthesized another PPV with a higher oxadiazole composition in the polymer backbone (POXO3-1, Chart 1) in hopes of further improving electron transporting properties. We also went in the other direction by synthesizing a polymer (POXO-C, Chart 1) which contains less oxadiazole in the main chain and furthermore contains carbazole in the side chain to improve the hole transporting ability of the polymer. In this paper, we report the synthesis and device performance of these two new polymers.

Experimental Section

The syntheses of compounds **IV**,[25] **V**,[26] **VII**,[26] and **IX**[25] have been reported previously. *p*-Divinylbenzene was purified according to a literature procedure.[27] All other chemicals were purchased from Aldrich Chemical Co. and used as received unless otherwise stated.

Compound VI. A mixture of carbazole (10.00 g, 0.06 mol), 1,6-dibromohexane (14.59 g, 0.06 mol), and K_2CO_3 (25.00 g,

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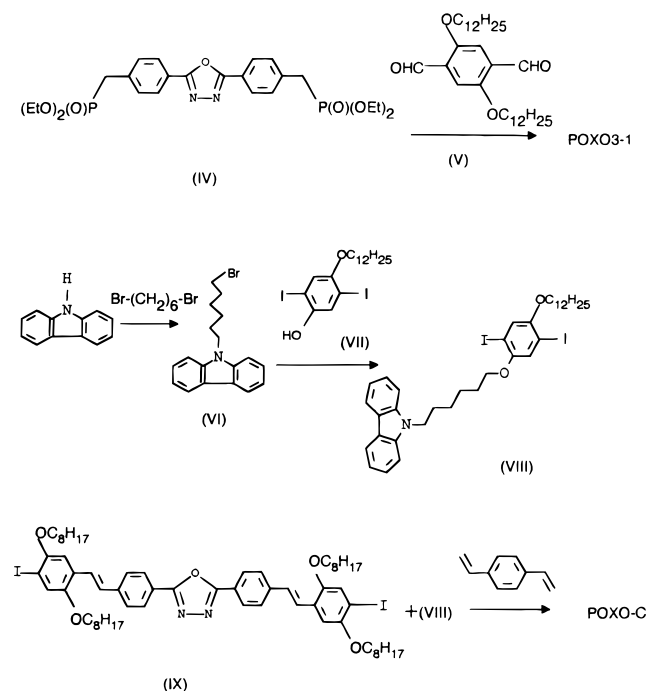(23) Schulz, B.; Kaminorz, Y.; Brehmer, L. *Synth. Met.* **1997**, *84*, 449.
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0.18 mol) in dimethylformamide (DMF) (20 mL) was stirred at room temperature overnight and was then poured into water. After extraction with methylene chloride, the organic layer was washed with water and dried over $MgSO_4$. The solvent was then evaporated. The resulting residue was purified by chromatography (methylene chloride as eluent) to give 5.60 g of product (yield, 28%; mp, 50−51 °C). ^{1}H NMR (CDCl₃, ppm): δ 1.32−1.45 (m, 4H, alkyl protons), 1.72−1.87 (m, 4H, alkyl protons), 3.32 (t, *J* = 6.67 Hz, 2H, −CH₂Br), 4.46 (t, *J* = 7.08 Hz, 2H, −NCH₂−), 7.22 (t, *J* = 7.52 Hz, 2H, aromatic protons), 7.36 (d, *J* = 8.23 Hz, 2H, aromatic protons), 7.45 (t, *J* = 7.54 Hz, 2H, aromatic protons), 8.01 (d, *J* = 7.62 Hz, 2H, aromatic protons).

Compound VIII. A mixture containing compound **VI** (0.87 g, 2.62 mmol), compound **VII** (1.39 g, 2.62 mmol), K_2CO_3 (0.40 g, 2.89 mmol), and DMF (5 mL) was stirred at 100 °C overnight and was then poured into water. The resulting aqueous solution was extracted with ether. The organic layer was washed with water and dried over $MgSO_4$. After evaporation of the solvent, the residue was purified by chromatography (hexane:ethyl acetate = 5:1 as eluent). The product was further purified by recrystalization from hexane (in the refrigerator) (yield, 1.13 g, 55%; mp, 54−55 °C). ^{1}H NMR (CDCl₃, ppm): δ 0.90 (t, *J* = 6.56, 3H, −CH₃), 1.30 (m, 16H, alkyl protons), 1.45−1.62 (m, 6H, alkyl protons), 1.80 (m, 4H, alkyl protons), 1.97 (quartet, *J* = 6.89 Hz, 2H, alkyl protons), 3.90 (m, 4H, −CH₂O−), 4.50 (t, *J* = 7.08 Hz, 2H, −NCH₂−), 7.12 (s, 1H, aromatic proton), 7.15 (s, 1H, aromatic proton), 7.22 (t, *J* = 7.52 Hz, 2H, aromatic protons), 7.36 (d, *J* = 8.23 Hz, 2H, aromatic protons), 7.45 (t, *J* = 7.54 Hz, 2H, aromatic protons), 8.01 (d, *J* = 7.62 Hz, 2H, aromatic protons). Anal. Calcd for $C_{36}H_{47}NO_2I_2$: C, 55.46; H, 6.08; N, 1.80. Found: C, 55.42; H, 6.06; N, 1.74.

POXO3-1. NaH (0.0690 g, 2.8700 mmol) was added into a solution of compound **IV** (0.5000 g, 0.9570 mmol) and THF (5 mL). To the resulting mixture was added dropwise a THF solution of compound **V** (0.4814 g, 0.9570 mmol in 7 mL of THF). The mixture was refluxed for 2 h and then poured into methanol. The polymer was collected by filtration and washed with water and then methanol. The crude polymer was redissolved in hot THF and reprecipitated from methanol to give 0.59 g of polymer as yellow powders (86%). ^{1}H NMR (CDCl₃, ppm): δ 0.88 (b, 12H, −CH₃ in alkoxy chain), 1.37 (b, 32H, alkyl protons), 1.57−1.92 (m, 8H, alkyl protons), 4.01 (b, 4H, −OCH₂−), 6.98 (s, 2H, aromatic protons), 7.16 (b, 2H, vinyl protons), 7.65 (m, 2H, vinyl protons), 7.68 (b, 4H, aromatic protons), 8.13 (b, 4H, aromatic protons). Anal. Calcd for $C_{48}H_{64}O_3N_2$: C, 80.40; H, 9.00; N, 3.91. Found: C, 79.87; H, 8.61; N, 3.68.

POXO-C: This polymer was synthesized under typical Heck coupling conditions.[19] The mole ratio of compounds **IX** to **VIII** is 2 to 1. ^{1}H NMR (CDCl₃, ppm): δ 0.90, 1.37, 1.53, 1.86, 4.00, 4.35, 7.20, 7.53, 7.65, 8.15. Anal. Calcd for $C_{63.36}H_{79.01}N_{1.67}O_4$: C, 82.00; H, 8.58; N, 2.52. Found: C, 79.86; H, 8.20; N, 2.28.

Characterization. The ^{1}H NMR spectra were collected on a Bruker 360 MHz FT NMR spectrometer. A HP 8453 UV/vis spectrometer was used to record the UV/vis spectra. Elemental analyses were performed by Robertson Microlit Laboratories, Inc.

To fabricate single layer LED devices, thin films were spin-coated from tetrachloroethane solutions of the polymers onto glass substrates coated with indium tin oxide. This produced a 900 Å polymer layer on top of the ITO. This thickness was the same for all of the polymers studied. A layer of aluminum (1000−2000 Å) was then deposited by vacuum evaporation to create many 1 mm² devices on a substrate. 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: 1 nA = 1.32 nW). No other corrections concerning the light loss through absorption, waveguiding, etc., were made. The photodiode detector was put as close to the

Scheme 1. Syntheses of the Monomers and Polymers

Figure 1. UV/vis spectra of the polymers in dilute THF solutions.

Figure 2. Fluorescence spectra of the polymers in THF solutions and as solid films.

Figure 3. Current–light–voltage characteristics for an (ITO/POXO3-1/Al) devices. Inset: Light vs current curve of the same device.

LED as possible (3 mm away), to collect a significant fraction of the light produced in the forward direction. All the fabrication (except for the cathode evaporation) and measurements were performed in air and at room temperature.

Results and Discussion

The polymer structures are shown in Chart 1. POXO3-1 was synthesized by the Horner–Wittig–Emmons (HWE) reaction (Scheme 1). To preserve reasonable solubility in organic solvents, this polymer was separated from the reaction mixture before it started to precipitate. POXO-C was synthesized by the Heck coupling reaction. The observation of a small broad peak at 4.35 ppm in the ^{1}H NMR of the polymer shows that the carbazole-containing monomer is indeed incorporated into the polymer. The number average molecular weights of POXO3-1 and POXO-C, measured by gel permeation chromatography using polystyrene as standards are 7000 and 13 000, respectively with a polydispersity of 2.6 for POXO3-1 and 2.2 for POXO-C.

Figure 1 shows the UV/vis spectra of the polymers in dilute THF solutions. Although the composition of the polymers differ significantly, their absorption spectra are very similar and comparable to alkoxy-PPV except that POXO3-1 shows much clearer vibronic features as shoulder peaks.[25] The oxadiazole ring and its adjacent phenyl rings appear not to be twisted significantly, since if this were the case, one would expect the absorption of POXO3-1 to be at shorter wavelengths than that of POXO-C or alkoxy-PPV.[25] The maximum absorption occurs at 450 nm for both polymers. The band gaps of POXO3-1 and POXO-C, calculated from the absorption band edges, are 2.46, and 2.44 eV, respectively.

The fluorescence spectra of the polymers in dilute solution and as solid films are shown in Figure 2. Both polymers have similar photoluminescence in solutions with emission peaks at 505 nm and a shoulder around 540 nm, similar to that of alkoxy-PPV. However,
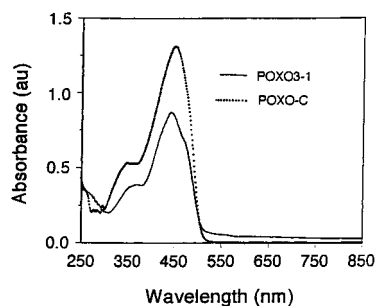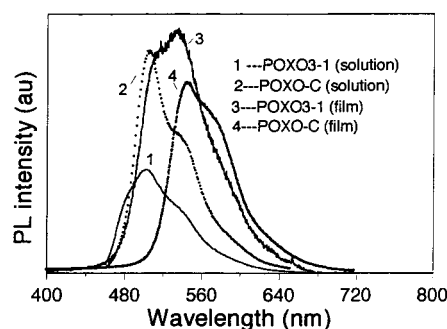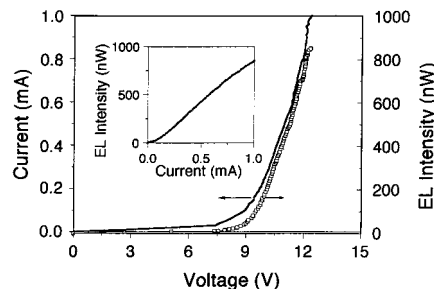
POXO3-1 also has another clear shoulder peak around 480 nm. As solid films, POXO3-1 and POXO-C have significantly different photoluminescence. In comparison with its solution photoluminescence, POXO-C as solid films has emissions red-shifted by almost 50 nm, due to aggregation in the films.[28] POXO3-1, however, shows a smaller red shift of about 35 nm. The onset wavelength of the emission for POXO3-1 is around 470 nm, while, for POXO-C, it is around 510 nm.

Both polymers showed good LED performance. The current–light–voltage characteristics of these polymer LEDs are shown in Figures 3 and 4. LED quantum efficiencies of 0.08% for POXO3-1 and 0.12% for POXO-C were obtained. Both values are significantly larger than that obtained in LEDs fabricated with the alkoxy-PPV.[25] The near linear relationship of light vs current for both polymers indicates that the light is produced by the combination of injected charges from both electrodes. The LED efficiencies obtained from these oxadiazole-containing polymers are among the highest values for

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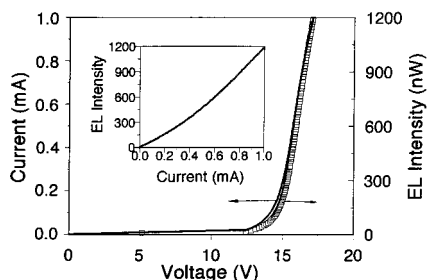
Figure 4. Current−light−voltage characteristics for an (ITO/POXO-C/Al) devices. Inset: Light vs current curve of the same device.

Figure 5. Typical cyclic voltammograms measured using Model 174A polarographic analyzer and Model 175 universal programmer (Princeton Applied Research) with scan rate of 200 mV/s.

Table 1. Electrochemical Potentials and Energy Levels of the Polymers

polymers	reduction potential (V vs FOC)[a]	bandgap[b] (eV)	HOMO[c] (eV vs vacuum)	LUMO[d] (eV vs vacuum)
POXO3-1	−2.22	2.46	−5.04	−2.58
POXO-C	−2.40	2.44	−4.84	−2.40
POXO5-1	−2.32	2.46	−4.94	−2.48
alkoxy-PPV	−2.42	2.44	−4.82	−2.38

[a] Reduction potentials were measured by cyclic voltammetry. [b] Bandgaps were calculated from the absorption spectra of the polymer solutions. [c] HOMO levels were estimated from the LUMO and energy gaps. [d] LUMO levels were converted from measured reduction potentials assuming the absolute energy level of ferrocene to be −4.8 eV.[18]

single layer polymer LEDs with the configuration of ITO/polymer/Al.[15] The improvement in efficiency is comparable to, if not larger than, that achieved in double layer devices using oxadiazole-containing polymers as electron injection layers.[20−22] For example, Pei and Yang[21] reported that single layer LEDs with a configuration of ITO/MEH−PPV/Al had an external quantum efficiency of only 0.002% (turn on voltage, 15 V). However, when an oxadiazole-containing polymer is used as the electron injection layer, the resulting double layer device showed external quantum efficiency of 0.08%. Similar improvement has been reported by other groups.[20−22] It is worth noting that, for those double layer devices using oxadiazole-containing polymers as electron injection layers, the turn-on voltages are usually higher than their corresponding single layer devices.[20−22,29] However, we found that introducing oxadiazole moieties into the PPV backbone did not increase the turn-on voltages of the resulting polymer LEDs. This is likely due to the conjugation of the oxadiazole rings with the PPV segments. The similar band gap and broad absorption band seen in POXO3-1 and the alkoxy-PPV indicates a comparable π-electron conjugation in both polymers. When calcium (over-coated with silver) was used as the cathode, similar turn-on voltages and slightly smaller efficiencies were obtained for POXO3-1 and POXO5-1. This result supports the hypothesis that electron injection is greatly improved by the introduction of oxadiazole units into the conjugated chain. We performed device fabrication and characterizations in air (except the vacuum deposition of cathodes) without taking any precautions. Higher quantum efficiency might be achievable with optimization of the fabrication conditions.

We believe the introduction of the oxadiazole into the conjugated main chain has two effects. One is to provide a site for electron injection, because it is relatively electron deficient. Although the oxadiazole is conjugated into the polymer backbone, the local electron density at oxadiazole is still less than that of other phenylenevinylene units. The other effect of oxadiazole on the main chain is to lower the energy level of the polymers (LUMO), thus facilitating electron injection and transport. Introducing oxadiazole into the side chain of a PPV polymer would only provide the first effect. Indeed, PPVs with oxadiazole on the side chains have a device efficiency 10 times less than that of the PPV polymer with oxadiazole in the main chain.[30]
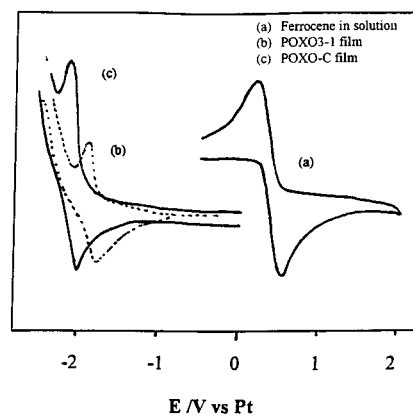
The effect of the oxadiazole on the Fermi levels of the polymers was studied by cyclic voltammetry (CV). A thin polymer film was cast onto a Pt disk working electrode (diameter = 2 mm). The counter and reference electrodes were both Pt wires. The experiment was carried out in anhydrous acetonitrile with tetrabutyl-ammonium tetrafluoroborate as the supporting electrolyte under a nitrogen atmosphere. The results were compared with a ferrocene/ferrocenium (FOC) couple measured in the same solution. Examples of typical cyclic voltammograms are shown in Figure 5 (scan rate was 200 mV/s). The oxidation processes of all four polymers are irreversible, and the polymer films become dark after one oxidation scan (0−2.5 V). The reduction potentials of the polymers vs ferrocene/ferrocenium are listed in Table 1. The lowest unoccupied molecular orbital (LUMO) levels versus the vacuum level are derived from the measured reduction potentials by assuming the energy level of FOC is 4.8 eV below the vacuum level.[18] The positions of the HOMO levels are estimated by subtracting the energy gap from their LUMO levels. It is worth mentioning that obtaining absolute HOMO and LUMO levels from electrochemical data in combination with the energy gap is still in debate, and attempting to compare the absolute HOMO/LUMO levels for different polymers reported in different papers may not be appropriate.[18,31] However, it should be valid to extract the relative trend of the energy levels

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of different polymers measured in the same conditions. From Table 1, it is clear that the higher the oxadiazole content, the lower the LUMO level of the polymer, and therefore the better the electron injection properties.

Surprisingly, however, POXO5-1 rather than POXO3-1 has the highest LED efficiency. One explanation is that the hole injection/transport is sacrificed when the oxadiazole content is too high, as in the case of POXO3-1. Since all four polymers have similar band gaps, the lower the LUMO of the polymer, the lower the HOMO, and therefore the larger the hole injection barrier. To test this claim, we fabricated double layer devices with the configuration of ITO/PPV/POXO3-1 or -5−1/Al. The PPV layer was thermally converted from its xanthate precursor as reported previously.[15] The double layer device based on POXO3-1 showed bright emission with an external efficiency of 0.07%, while the double layer device based on POXO5-1 has an external efficiency of only 0.01%. This result indicates that POXO3-1 is a better electron injector/transporter but worse hole injector/transporter than POXO5-1. It is worth mentioning that we did not focus on getting quantum efficiencies as high as possible in double layer devices but rather focused on the relative results for POXO3-1 and POXO5-1 at similar fabrication conditions. There is clearly a tradeoff between electron injection/transport ability and hole injection/transport ability. Finding the optimal polymer composition is therefore essential for high efficiency with low operation voltages.

In comparison with POXO5-1, POXO-C shows similar LED performance. It seems that introducing carbazole into the side chain has no significant effect on the hole transport ability of the polymer. One explanation is that the polymer backbone itself has good enough hole transport ability. Since the oxadiazole content is very low, the HOMO of the polymer backbone is not perturbed very much. From the CV data, the HOMO of POXO-C is actually very close to that of the alkoxy-PPV. The other reason could be that the carbazole content is too low. To form an efficient charge transport pathway, a minimum concentration of carbazole may be needed (percolation threshold).

Conclusion

We have synthesized polymers with bipolar transport abilities. It is shown that putting the electron transporting (ET) and hole transporting (HT) units in conjugation with an emissive polymer improves the bipolar transport properties. The ET/HT ratio has to be carefully adjusted to maintain balanced charge injection. Previous research has combined these functions in one polymer but not in conjugation. Our research demonstrated that this approach is viable and can significantly improve device performance. Since there are many other efficient electron-transporting moieties[29] which could be introduced into the conjugated backbone, we expect many new polymers with good LED performance to be developed in the future.