# Novel Electroluminescent Polymers Derived from Carbazole and Benzothiadiazole

**Jian Huang, Yuhua Niu, Wei Yang, Yueqi Mo, Ming Yuan, and Yong Cao***

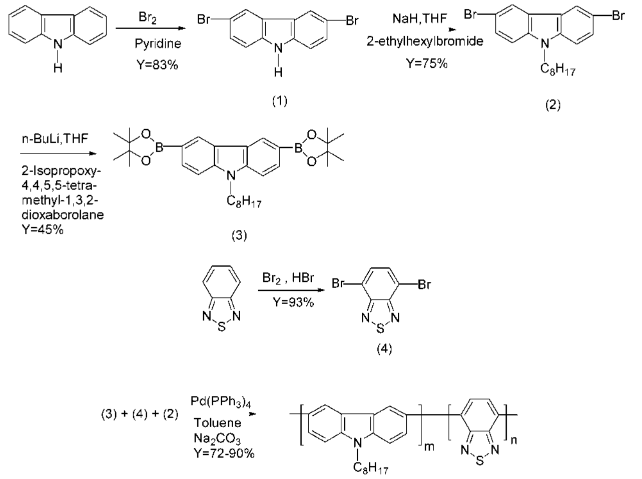
*Institute of Polymer Optoelectronic Materials and Devices, South China University of Technology, Guangzhou, China 510640*

*Received March 5, 2002*
*Revised Manuscript Received April 27, 2002*

**Introduction.** Polymer electroluminescent diodes have attracted much attention because of potential application in large-area flat panel display at low power consumption. Since the discovery of electroluminescence (EL) for polyphenylenevinylene (PPV) in 1990,[1] remarkable efforts have been made for developing new EL-conjugated polymers.[2,3] Recently, increasing interest have been paid to carbazole-based polymers because of their optical properties and good hole-transporting ability in light-emitting devices.[4,5] Among them most widely used and investigated was poly(vinylcarbazole) (PVK)−nonconjugated vinyl polymer with carbazole attached as a side chain. Light-emitting devices with PVK as a host and with a narrow band laser dye as a guest were widely studied.[6] Only a few reports were attributed to conjugated polymer with carbazole as a main chain built unit.[7] Since exciton transfer and trapping between the chromophoric segments are a much faster process than radiative and nonradiative decay, energy transfer from a wide gap segment to a narrow gap site should be highly efficient.[7b] Considering that conjugated polymer polycarbazole (PCz) could have as good hole-transport properties as PVK, it would be advantageous if we could use it as a host segment in copolymerization with various narrow band gap comonomers. Homopolymers of carbazole[7,11] and benzothiadiazole[8] have been reported. In this communication, we present our results on the preparation of a novel carbazole-based copolymers, poly(4,7-(2,1,3-benzothiadiazole)-3,6-(*N*-(2-ethylhexyl)carbazole)) (PCzBTDZ), prepared via palladium-catalyzed Suzuki coupling reaction. Efficient energy transfer from blue light-emitting carbazole segments to the benzothiadiazole unit occurred, and efficient orange-red light emission due to the benzothiadiazole unit was observed.

**Results and Discussion.** The synthesis route is shown in Scheme 1. 3,6-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-ethylhexylcarbazole (**3**) has been prepared in three steps. First, carbazole (Aldrich) was mixed with bromine in a mixture of carbon bisulfide and pyridine solution to give 3,6-dibromocarbazole (**1**) in a 83% yield. Then the alkylation of the nitrogen atom of 3,6-dibromocarbazole in THF by NaH and 2-ethylhexyl bromide leads to 3,6-dibromo-9-ethylhexylcarbazole (**2**) in a 75% yield.[9] Finally, 3,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-ethylhexylcarbazole (**3**) is prepared from 3,6-dibromo-9-ethylhexylcarbazole upon reaction with *n*-BuLi and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane in anhydrous THF. To a mixture of 2,1,3-benzothiadiazole and 47% hydrobromic acid, we added bromine under reflux for 2.5 h to give 4,7-dibromo-2,1,3-benzothiadiazole (**4**).[10] All these compounds have been characterized by NMR spectroscopy.

### Scheme 1



Homopolymer and copolymers are prepared from a Suzuki coupling reaction between dibromic functionalized aromatic units and 3,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-ethylhexylcarbazole. All these polymerization reactions show a yield between 72% and 90%.

Up to date conjugated main-chain polymers of carbazole were prepared either via electrocatalyzed dehalogenative polycondensations of 9-alkyl-3,6-dibromocarbazoles in the presence of nickel catalysts[7b] or via the nickel-catalyzed[7a] or palladium-catalyzed[11] cross-coupling reaction of 9-alkyl-3,6-dibromocarbazole or chemical oxidation of comonomers. To our knowledge, we are the first group that prepared conjugated carbazole homopolymer and copolymers by Suzuki coupling. Suzuki coupling is a prevalent methods for the synthesis of polyarylenes and polyheterocycles because it is tolerant of most functionalities and proceeds under mild condition.[12] Another advantage of Suzuki coupling is that it allows to obtain an alternating copolymers in the case of A−B type of copolymer, while cross-coupling of dibromides provides multiblock copolymer. In the case of Suzuki coupling, the narrow band gap component can be separated from both sides by the wide band gap segment once the ratio of former to later is equal to one unit or less. As a result, it will allow the most efficient trapping, thereby the most efficient energy transfer.

The resulting copolymers are soluble in common organic solvents. The number-average molecular weights of these copolymers, PCzBTDZ1, PCzBTDZ5, PCzBTDZ15, PCzBTDZ30, PCzBTDZ40, and PCzBTDZ50 (where 1, 5, 15, 30, 40, and 50 indicate the feed molar content of BTDZ monomer in the copolymers), are 4300, 3800, 3600, 4000, 4300, 2500, respectively with a polydispersity of around 1.5 with THF as eluent using polystyrene standards.

The UV−vis absorption and photoluminescence (PL) spectra for the copolymers in thin films are shown in Figure 1. As shown in Figure 1, except PCzBTDZ1, we can clearly observe the appearance of the absorption bands of BTDZ segments centered at about 465 nm. For PCzBTDZ1 it is hard to detect the 465 nm absorption, probably due to the low sensitivity of the spectropho-

---

* To whom correspondence should be addressed. E-mail: poycao@scut.edu.cn.

10.1021/ma0255130 CCC: $22.00

**Table 1. Physical Data for the Polymers[a]**

| polymer | $E_{ox}$ (V) | HOMO (eV) | $E_{red}$ (V) | LUMO (eV) | $E_g$ (eV) | $E_g{}^b$ (eV) | $PL_{eff}$ (%) | $EL_{eff}$ (%) |
|---|---|---|---|---|---|---|---|---|
| PCz | 0.85 | −5.25 | −2.40 | −2.00 | 3.25 | 3.18 | 3.6 | 0.0014 |
| PCzBTDZ1 | 0.90 | −5.30 | | | | | 63.9 | 0.01 |
| PCzBTDZ5 | 0.90 | −5.30 | −1.40 | −3.00 | 2.30 | 2.28 | 43.4 | 0.02 |
| PCzBTDZ15 | 0.93 | −5.33 | −1.37 | −3.03 | 2.30 | 2.30 | 44.2 | 0.20 |
| PCzBTDZ30 | 1.00 | −5.40 | −1.28 | −3.12 | 2.28 | 2.26 | 13.9 | 0.40 |
| PCzBTDZ40 | 0.90 | −5.30 | −1.30 | −3.10 | 2.20 | 2.29 | 11.7 | 0.48 |
| PCzBTDZ50 | 1.00 | −5.40 | −1.30 | −3.10 | 2.30 | 2.28 | 12.0 | 0.43 |

[a] Poly(carbazole-*co*-benzothiadiazole) with different compositions were synthesized from various [HCz]/[BTDZ] starting molar ratios: 99:1 (PCzBTDZ1); 95:5 (PCzBTDZ5); 85:15(PCzBTDZ15); 70:30 (PCzBTDZ30); 60:40 (PCzBTDZ40); 50:50 (PCzBTDZ50). [b] Calculated from onset of 465 nm absorption peaks.

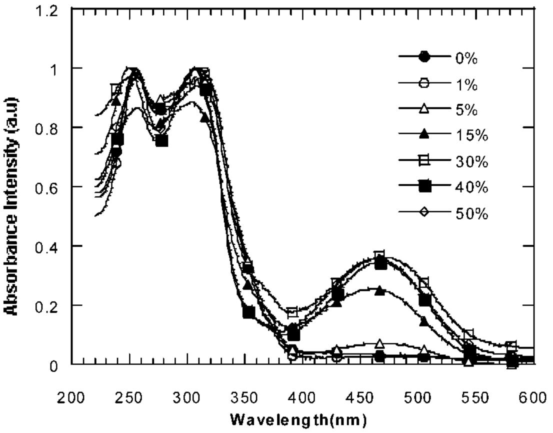


**Figure 1.** UV-visible absorption spectra of PCz and HCz-*co*-BTDZ copolymers in thin film.

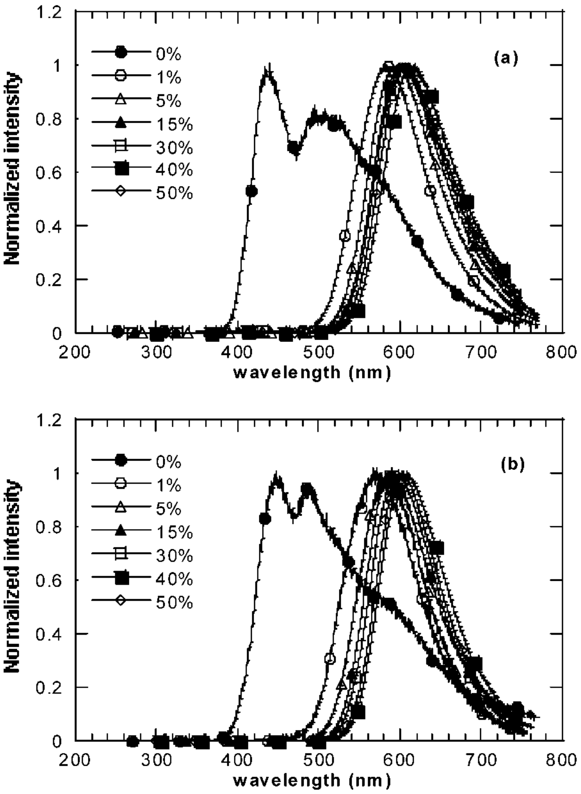


**Figure 2.** (a) Normalized PL spectra of PCz and HCz-*co*-BTDZ copolymers in the solid state. (b) Normalized EL spectra of devices from PCz and HCz-*co*-BTDZ copolymers.

tometer. Figure 2a shows PL spectra of PCz homopolymer and PCzBTDZ copolymers under 325 nm excitation from HeCd laser. Emission of the Cz segment was completely quenched for copolymers with a BTDZ concentration as low as 1% of it. This fact indicates that the trapping of exciton by BTDZ unit is very efficient. As a result, the excitation energy on the Cz segments was transferred to the BTDZ unit with very high efficiency. PL peaks were red-shifted with increasing BTDZ content in the polymer. In Table 1, we listed PL efficiencies obtained with 325 nm excitation for the PCz homoppolymer and 442 nm excitation for copolymers, respectively, using a HeCd laser. It is worthy to note that PCzBTDZ copolymers exhibited very high PL efficiency from 63.9% PCzBTDZ1 going down gradually to 12% for 40−50% BTDZ content. This fact seems to support trapping mechanism for such a wide−narrow band gap copolymer system.

The redox behavior of the polymers were investigated by cyclic voltammetry (CV). The results are summarized in Table 1. All the copolymers have similar energy gaps of about 2.3 eV. The energy gaps calculated from the electrochemical p-doping and n-doping onset potentials are consistent with the optical energy gaps deducted from absorption spectra. The HOMO levels of homopolymer poly(3,6-(*N*-(2-ethylhexyl)carbazole)) and BTDZ copolymers are about −5.3 eV which is at least 0.5 eV lower than that of PVK.[6a,13]

Figure 2b shows the normalized EL spectra of the homopolymer and copolymers. Device configuration is the following: ITO/PEDT:PSS/polymer/Ba/Al. The EL spectra of all the copolymers are nearly identical to the PL spectra. Despite the significant decrease of the photoluminescence quantum efficiencies, EL efficiencies increase with BTDZ contents. Here, 0.4−0.5% external quantum efficiencies of orange-red emission can be obtained from devices with copolymers with BTDZ content equal to or higher than 30%. It is clear from Table 1 that the quantum efficiency in such devices is limited by the electron injection. With inserting BTDZ units into polymers the electron injection significantly improved due to lowering the LUMO level for copolymers (3.0−3.1 eV, Table 1). Significant improvement of device efficiencies for copolymers with a BTDZ content larger than 30% may result from improved electron transport due to enhanced interchain interaction in high BTDZ content copolymers. Optimizations of the electron injection are ongoing by modification of polymer/cathode interface.

**Conclusion.** We have synthesized a series of novel carbazole-based PCzBTDZ copolymers with different BTDZ content by a Suzuki-coupling reaction. The efficient energy transfer due to exciton trapping on narrow band gap BTDZ sites has been observed. Preliminary device characteristics are promising. Conjugated carbazole segment provides good hole injection and hole-transport properties. Electron injection is greatly enhanced by the insertion of BTDZ units. The use of conjugated polycarbazole as wide band gap segment could provide a new way to combine good hole-injection properties along with color turning ability. Synthesis of an entirely new class of polycarbazole-based main chain copolymers with varieties of aromatic rings and heterocycles by Suzuki coupling reaction are in progress.

**Acknowledgment.** This work is supported by the National Natural Science Foundation of China (Project No29992530-6) and Guangdong Province Grand (No. 990623).

**Supporting Information Available:** Text giving details of all synthetic and purification steps and $^1$H NMR and $^{13}$C NMR data of all the compounds (compounds **1**−**4**), a table giving elemental analysis data, and a figure showing CV curves of some of the polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

## References and Notes

(1) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R. *Nature (London)* **1990**, *347*, 539.

(2) Segura, J. L. *Acta Polym.* **1998**, *49*, 319.

(3) Friend, R. H.; Gymer, R. W.; Holmes, A. B. *Nature (London)* **1999**, *397*, 121.

(4) (a) Lee, J. H.; Park, J. W.; Ko, J. M.; Chang, Y. H. *Polym. Bull. (Berlin)* **1993**, *31*, 339. (b) Justin Thomas, K. R.; Lin Jiann, T. *J. Am. Chem. Soc.* **2001**, *123*, 9404.

(5) (a) Lee, J. H.; Park, J. W.; Choi, S. K. *Synth. Met.* **1997**, *88*, 31. (b) Meng, H.; Chen, Z. K. *J. Phys. Chem. B* **1999**, *103*, 6429. (c) Chao, C. S.; Whang, W. T. *Macromol. Chem. Phys.* **2001**, *202*, 2864.

(6) (a) Kido, J.; Hongawa, K.; Okuyama, K.; Nagai, K. *Appl. Phys. Lett.* **1994**, *64*, 815. (b) Zhang, C.; Seggern, H. V.; Schmidt, H. W.; Heeger, A. J. *Synth. Met.* **1995**, *72*, 185. (c) G-Thianche, E.; Sentein, C.; Lorin, A.; Denis, C.; Raimond, P.; Nunzi, J. M. *J. Appl. Phys.* **1998**, *83*, 4236.

(7) (a) Romeo, D. B.; Schaer, M.; Leclerc, M.; Ades, D.; Siove, A.; Zuppiroli, L. *Synth. Met.* **1996**, *80*, 271. (b) Lmimouni, K.; Legrand, C.; Chapoton, A. *Synth. Met.* **1998**, *97*, 151 (c) Morin, J.-F.; Leclerc, M. *Macromolecules* **2001**, *34*, 4680.

(8) Kanbana, T.; Yamamoto, T. *Chem. Lett.* **1993**, 419.

(9) Kim, J. K.; Hong, S. I.; Cho, H. N. *Polym. Bull. (Berlin)* **1997**, *38*, 169.

(10) Kurt, P.; Mike, Z.; Richard, S. *J. Heterocycl. Chem.* **1970**, *6*, 629.

(11) Iraqi, A.; Wataru, I. *Synth. Met.* **2001**, *119*, 159.

(12) Goodson, F. E.; Wallow, T. I.; Novak, B. M. *Macromolecules* **1998**, *31*, 2047.

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

MA0255130