

SYNTHESIS AND CHARACTERIZATION OF NOVEL BIPOLAR PPV-BASED COPOLYMER CONTAINING TRIAZOLE AND CARBAZOLE UNITS*

Ze Liu, Li-xiang Wang**, Xia-bin Jing and Fo-song Wang

*The State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry,
Chinese Academy of Sciences, Changchun 130022, China*

Abstract Two new blue light-emitting PPV-based conjugated copolymers containing both an electron-withdrawing unit (triazole-TAZ) and electron-rich moieties (carbazole-CAR and bicarbazole-BCAR) were prepared by Wittig condensation polymerization between the triazole diphosphonium salt and the corresponding dialdehyde monomers. Their structures and properties were characterized by FT-IR, TGA, DSC, UV-Vis, PL spectroscopy and electrochemical measurements. The resulting copolymers are soluble in common organic solvents and thermally stable with a T_g of 147°C for TAZ-CAR-PPV and of 157°C for TAZ-BCAR-PPV. The maximum photoluminescence wavelengths of TAZ-CAR-PPV and TAZ-BCAR-PPV film appear at 460 nm and 480 nm, respectively. Cyclic voltammetry measurement demonstrates that TAZ-BCAR-PPV has good electrochemical reversibility, while TAZ-CAR-PPV exhibits the irreversible redox process. The triazole unit was found to be an effective π -conjugation interrupter and can play the rigid spacer role in determining the emission colour of the resulting copolymer.

Keywords Light-emitting polymer, PPV-based bipolar polymer, Triazole-containing polymer, Carbazole-containing polymer

INTRODUCTION

Since the first discovery of the polymer light-emitting diodes (PLED) based on poly(*p*-phenylene vinylene) (PPV) by Burroughes *et al.* at Cambridge^[1], a number of conjugated polymers such as polythiophene (PTs), poly(*p*-phenylene) (PPPs) and poly(alkylfluorene) (PFs) have been synthesized and tremendous progress in this area has been achieved. For fabricating the PLED device with good performance, it is desirable to reach a balance of electron and hole injection. However, for most conjugated polymers, *p*-doping (hole injection) is more favorable than *n*-doping (electron injection), which usually causes the imbalance of hole injection and electron injection^[2, 3]. To solve this problem, a multilayer structure which was overlaid with an electron-transporting layer was usually employed. However, the fabrication of this multilayer PLED device is difficult and complicated. So it is desirable to design and synthesize a bipolar conjugated polymer with both electron and hole transporting ability for single-layer PLED^[4–7]. Although the three primary colours have been demonstrated in PLEDs, only red and green PLEDs have sufficient efficiencies and lifetimes to be of practical value^[8, 9]. Therefore, highly efficient blue-emitting conjugated polymers are requisite for full colour display application. Blue emission, which is difficult to achieve with inorganic semiconductors, has been found in several conjugated polymers with large energy band gaps such as poly(*p*-phenylene) (PPPs), poly(alkylfluorene) (PFs) and copolymers containing

* This work was supported by the National Natural Science Foundation of China (No. 29725410 and 29992530) and Chinese Academy of Sciences (KJ 951-A1-501-01).

** Corresponding author: Li-xiang Wang (王利祥), E-mail: lixiang@ns.ciac.jl.cn

Invited lecture at the International Workshop on Polymer and Organic Opto-Electronic Materials and Devices, May 13–15, 2001, Guangzhou, China

Received July 9, 2001

confined conjugated segments such as TRIDSB^[10], O-PMEH-PPV^[11], PMOX-CAR^[7].

In this paper, we describe on the design, synthesis and characterization of two new blue light-emitting PPV-based copolymers containing triazole and carbazole moieties as the electron and hole units. The alternating copolymers were prepared by Wittig condensation polymerization between the triazole diphosphonium salt and the dialdehyde monomers of carbazole (CAR) and bicarbazole (BCAR), respectively. The triazole unit has been incorporated into polymers because of its rigid character, which provides unusual physical and thermal properties, and has been used as an electron transporting material and a thermally stable and blue emitting material^[12–15]. The carbazole unit was also known as a hole-transporting and blue electroluminescent material^[7, 16, 18]. The combination of triazole and carbazole moieties into the PPV-based conjugated polymer backbone is expected to provide highly efficient blue emitting polymers with improved thermal stability, processability and charge transporting properties.

EXPERIMENTAL

Characterization

NMR spectra were collected from a Varian 400 MHz spectrometer with chloroform-*d* and DMSO-*d*₆ as solvents and tetramethylsilane as internal standard. FT-IR spectra were recorded on a Bio-Rad FTS 135 spectrometer using KBr pelleted samples. UV-Vis and fluorescence spectra were obtained with a Varian Cray 50 spectrophotometer and a Perkin-Elmer LS 50B luminescence spectrometer, respectively. Thermogravimetric analysis (TGA) was conducted on a Perkin-Elmer TGA 7 thermal analysis system with a TGA 2950 thermogravimetric analyzer with a heating rate of 10 K/min and under N₂ atmosphere. Differential scanning calorimetry (DSC) was run on the Perkin-Elmer DSC 7 thermal analysis system. Cyclic voltammetry (C-V) was performed on an EG&G Model 283 potentiationstat system with a three-electrode cell filled with a solution of Bu₄NClO₄ (0.1 mol/L) in acetonitrile at a scanning rate of 50 mV/s. The polymer films were coated on a square Pt electrode (0.5 cm²) by dipping the electrode into the corresponding solutions and then dried in air. A Pt electrode was used as the reference electrode, and an Ag/AgCl (0.1 mol/L) electrode was used as the reference electrode. Prior to each series of measurements the cell was purged with argon. Gel permeation chromatography (GPC) was conducted on a Waters 510 system using polystyrene as the standard and THF as the eluent.

Materials

Hexane and chloroform were distilled over calcium hydride. Absolute ethanol was obtained by distillation over magnesium. *o*-Dichlorobenzene, chlorobenzene, *N,N*-dimethylformamide (DMF) and *N*-methylpyrrolidone (NMP) were dried over 4A molecular sieves. 1-Bromododecane, methanol and triphenylphosphine were purchased from Acros and used without further purification. Phosphorus trichloride was used as received. Aniline was distilled prior to use.

Bis(4-methylphenyl)hydrazine (1)

A mixture of 2.1 g (20.0 mmol) hydrazine dihydrochloride and 6.8 g (44 mmol) *p*-toluoyl chloride was dissolved in NMP. The reaction was carried out in the presence of pyridine (5.0 mL) at 50°C for 3 h. The reaction mixture was poured into cold water and the precipitate was collected and dried in a vacuum oven. The pure white solid product was obtained by recrystallizing from methanol. The product yield was 4.07 g (76%). mp 257–259°C. ¹H-NMR (DMSO-*d*₆, δ): 10.4 (s, 2H), 7.8 (d, 4H), 7.3 (d, 4H), 2.3 (s, 6H). Elemental analysis (%): Calcd. for C₁₆H₁₆N₂O₂: C 71.62, H 6.01, N 10.44; found: C 71.28, H 5.96, N 10.59.

4-Phenyl-3,5-bis-[(4'-methyl)phenyl]-1,2,4-triazole (2)

To a solution of 5.58 g (0.06 mol) aniline in 20 mL of *o*-dichlorobenzene was slowly added 0.96 mL (0.011 mol) phosphorus trichloride. After the addition of 2.36 g (0.01 mol) of compound 1, the mixture was stirred and refluxed for 3 h at 200°C under nitrogen atmosphere. After cooling, the product was collected and digested in hot water and was then purified by crystallization from methanol. The product yield was 1.8 g (56%). mp 305°C. ¹H-NMR(CDCl₃, δ): 7.43 (m, 3H), 7.30 (d, 4H), 7.15 (d, 2H), 7.09 (d, 4H), 2.32 (s, 6H). Elemental analysis (%):

Calcd. for $C_{22}H_{19}N_3$: C 81.23, H 5.85, N 12.92; found: C 81.12, H 5.90, N 12.98.

4-Phenyl-3,5-bis-(4'-chloromethyl)phenyl]-1,2,4-triazole (3)

A mixture of 3.21 g (10 mmol) compound **2** and 3.15 g (2.3 equiv) of SO_2Cl_2 was dissolved in chlorobenzene. A catalytic amount of benzoyl peroxide was added as an initiator. The reaction mixture was refluxed at 90°C for 6 h under nitrogen atmosphere. The solvent was removed using a rotary evaporator. The crude product was purified by recrystallization with methanol. The yield was 1.87 g (48%). mp 197°C. ^1H -NMR ($CDCl_3$, δ): 7.49 (m, 3H), 7.40 (d, 4H), 7.32 (d, 4H), 7.18 (dd, 2H), 4.55 (s, 4H). Elemental analysis (%): Calcd. for $C_{22}H_{17}N_3Cl_2$: C 67.00, H 4.31, N 10.65; found: C 66.87, H, 4.28, N 10.69.

4-Phenyl-3,5-bis-(4'-tolylene-tributylphosphonium chloride)-1,2,4-triazole (4)

A solution consisting of 1.72 g (4.42 mmol) compound **3** and 2.68 g (13.26 mmol) tributylphosphine in 30 mL of DMF was stirred and heated to reflux for 24 h. The resulting mixture was poured into diethyl ether. After filtration and vacuum drying, the monomer was obtained as pale green solid. The yield of product was 2.53 g (72%). ^1H -NMR ($CDCl_3$, δ): 7.52–7.09 (m, 13H), 4.39 (d, 4H), 2.35 (d, 4H), 1.43 (s, 24H), 0.91 (s, 18H). Elemental analysis (%): Calcd for $C_{46}H_{71}N_3P_2Cl_2$: C 63.15, H 8.89, N 5.26; found: C 63.87, H 8.28, N 5.69.

The monomer **5** and **6** were synthesized according to the procedure described in literature^[16].

The polymerization was carried out through the Wittig condensation reaction between monomer **4** and monomer **5** or **6**, respectively.

Typical polymerization condition is as follows: A solution of sodium ethoxide (0.27 g, 4 mmol) in 5 mL absolute ethanol was added to 15.0 mL anhydrous chloroform/ethanol solution containing 0.58 g (1 mmol) salt of monomer **4** and (1 equiv) of the dialdehyde monomer **5** or **6** at room temperature. The mixture was stirred for 6 h under N_2 atmosphere. After reaction the mixture was extracted with excess chloroform and washed with 1 mol/L HCl and water. A crude polymer product was obtained by precipitation in methanol. Then, the polymer was dissolved in chloroform and precipitated with methanol for several times. After filtration and vacuum drying, yellowish TAZ-CAR-PPV (0.35 g, 56%) and TAZ-BCAR-PPV (0.40 g, 44%) were obtained, respectively^[17].

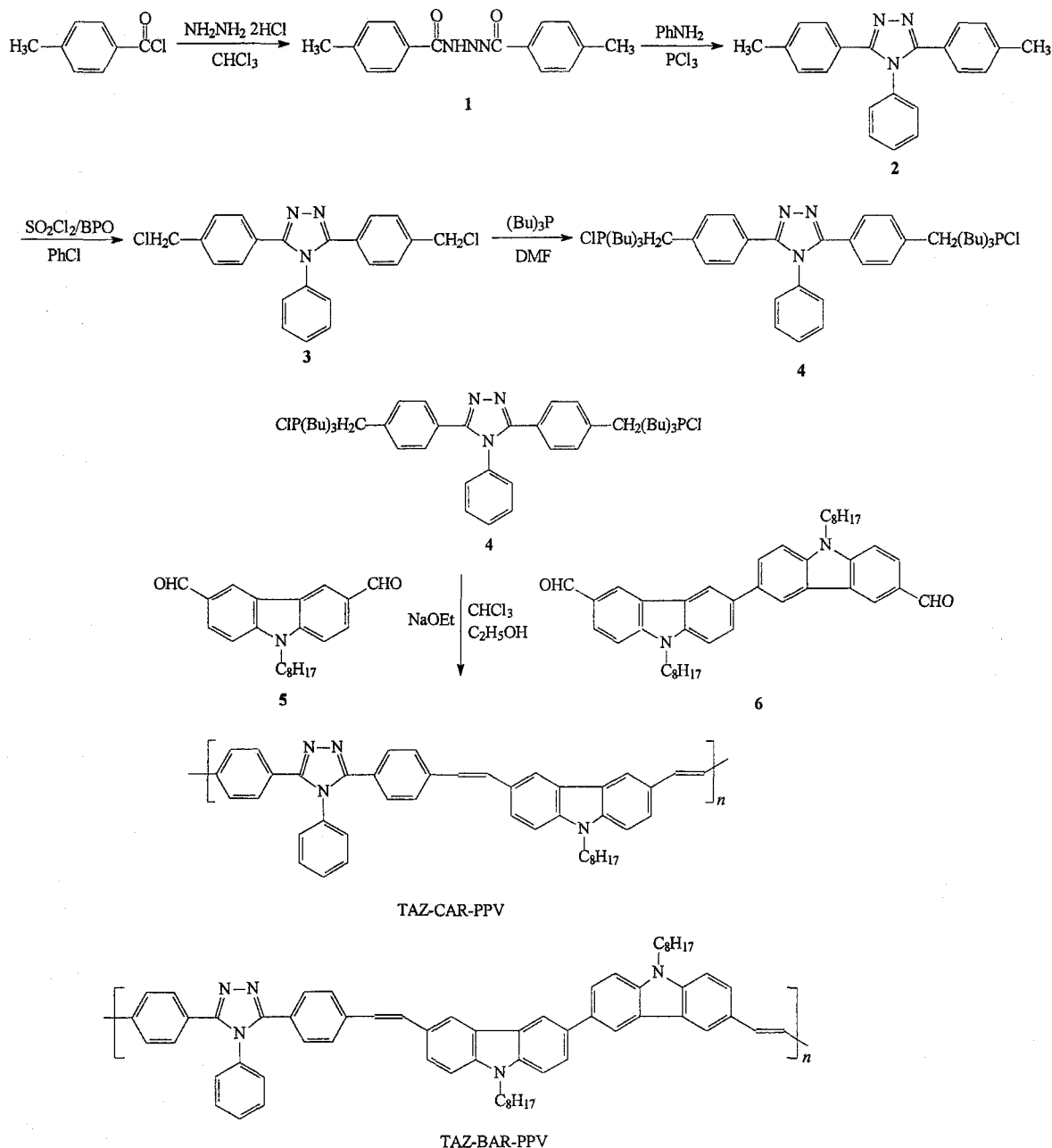
RESULTS AND DISCUSSION

Synthesis and Characterization

The synthetic routes to TAZ-CAR-PPV and TAZ-BCAR-PPV are shown in Scheme 1. Monomer **4** was synthesized from *p*-methylphenyl acid which was first reacted with thionyl chloride to form *p*-methylbenzoyl chloride. It then reacted with hydrazine dihydrochloride in pyridine to yield bis(4-methylphenyl)hydrazine (**1**) (yield 76%). The ring-closure reaction of **1** with aniline in the presence of phosphorus trichloride at reflux temperature was carried out to yield 4-phenyl-3,5-bis-[(4'-methyl)phenyl]-1,2,4-triazole (**2**) (56% yield), followed by chloromethylation with SO_2Cl_2 and then converted into the corresponding tributylphosphine salt by reaction of (**3**) with excess tributylphosphine. It should be pointed out that the key intermediate in the synthesis is (**3**). In fact, we failed to synthesize the compound (**3**) by the bromomethylation reaction of compound (**2**) with *N*-bromosuccinimide (NBS) in CCl_4 , which is useful for the oxadiazole^[7]. Its chloromethylation in CCl_4 with SO_2Cl_2 in the presence of benzoyl peroxide as an initiator produced the (**3**) in the form of a white crystal in good yield. Figure 1 shows the FT-IR spectra of the dialdehyde monomer **6** and TAZ-BCAR-PPV. The spectrum of the dialdehyde monomer exhibited a strong peak at 1685 cm^{-1} , which can be assigned to the aldehydic carbonyl group and another characteristic peak of aldehydic hydrogen at 2720 cm^{-1} . After polymerization, these two absorption bands disappear and a new weak peak appears at 960 cm^{-1} , corresponding to the out-of-plane vibration of the *trans*-vinylene units. From the above results, we can conclude that the polymerization reaction has taken place and the double bonds of the resulting polymer are mainly in the *trans* configuration, as expected.

Both TAZ-CAR-PPV and TAZ-BCAR-PPV are yellowish powders, and are soluble in common organic solvents such as chloroform and tetrahydrofuran. Their M_w were determined to be 7900 (polydispersity index of 1.2) for TAZ-CAR-PPV and 9000 (polydispersity index of 1.4) for TAZ-BCAR-PPV. The decomposition temperatures of the two polymers are higher than 440°C but their glass transition temperatures (T_g) are different,

147°C for TAZ-CAR-PPV and of 157°C for TAZ-BCAR-PPV, indicating that the incorporation of the triazole building block into the polymer backbone significantly enhances the thermal stability of the resulting polymers. Their T_g values are higher than that of analogues having carbazole moiety such as poly(*N*-octyl-3,6-carbazolyene) (60°C)^[18], PCPV (85°C)^[18], PMOX-CAR (98°C)^[7] and PPOX-CAR(130°C)^[7]. This difference may be ascribed to the effect of the introduction of triazole into the polymer^[15], leading to the increase of the rigidity of the polymer backbone. Compared with TAZ-CAR-PPV, TAZ-BCAR-PPV has a slightly higher T_g and decomposition temperature, indicating that the biphenylene moiety in the carbazole dimer increases the rigidity of the polymer main chain.



Scheme 1 Synthetic routes to the monomer 4 and copolymers

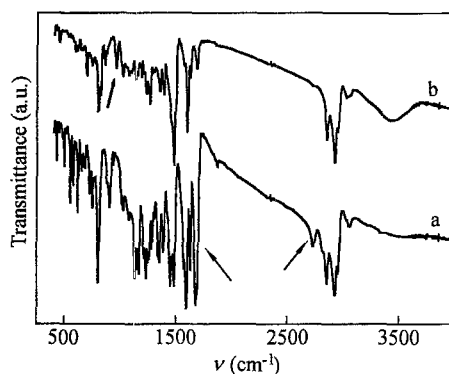


Fig. 1 FT-IR spectra of monomer 6 (a) and TAZ-BCAR-PPV (b)

Optical Properties

Both polymers emit blue light on irradiation with UV light. Figures 2 and 3 show the UV-Vis and photoluminescent spectra of TAZ-CAR-PPV and TAZ-BCAR-PPV, respectively. The UV-Vis absorption spectrum of TAZ-CAR-PPV in solution has three strong absorption peaks at 250, 280 and 350 nm, which can be attributed to the TAZ, CAR and π - π^* transition of the conjugated polymer^[7]. The UV-Vis absorption spectrum of TAZ-BCAR-PPV is similar to that of TAZ-CAR-PPV, except that the maximum absorption peak of carbazole dimer and conjugated backbone appear at 300 and 365 nm^[18]. These red shifts caused by carbazole dimer demonstrate that TAZ-BCAR-PPV has much effective conjugation length than TAZ-CAR-PPV, which is in agreement with its chemical structure. The band gaps taken from the onset of the absorption spectra are 2.75 eV for TAZ-CAR-PPV and 2.72 eV for TAZ-BCAR-PPV, respectively.

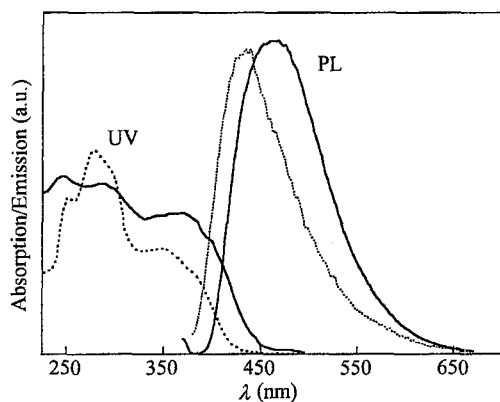


Fig. 2 UV-Vis and Photoluminescence spectra of TAZ-CAR-PPV solid thin film (—) and solution (-----)

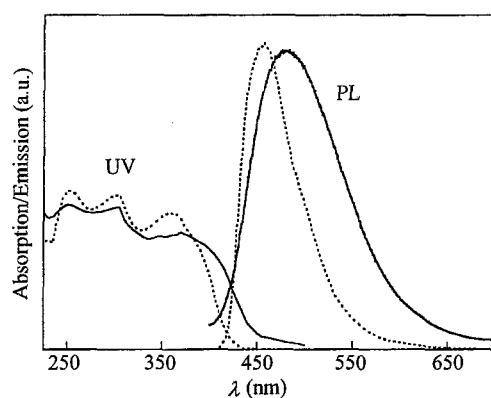


Fig. 3 UV-Vis and Photoluminescence spectra of TAZ-BCAR-PPV solid thin film (—) and solution (-----)

The PL spectrum of TAZ-CAR-PPV has maximum peaks at 437 (in solution) and 460 nm (as film), corresponding to pure blue light emission. Similarly, TAZ-BCAR-PPV exhibits quite identical spectral behavior with TAZ-CAR-PPV, its maximum peaks appear at 450 (in solution) and 480 nm (as film), indicating that TAZ-BCAR-PPV also emits blue colour in film. For each polymer, a red shift of about 30 nm is caused by the aggregation of conjugated polymer. The red shift of TAZ-BCAR-PPV compared to TAZ-CAR-PPV suggests that the incorporation of carbazole dimer into the polymer backbone will extend the conjugation length of the resulting copolymer. This result is consistent with that of the above UV-Vis measurement. Compared with similar bipolar conjugated polymer PPOX-CAR containing oxadiazole and carbazole moieties ($\lambda_{\text{pl}} = 495 \text{ nm}$)^[7], their

emission peak is blue-shifted by 35 nm for TAZ-CAR-PPV and by 15 nm for TAZ-BCAR-PPV, implying that the triazole unit is also an effective π -conjugation interrupter and can act as the rigid spacer role in determining the emission colour of the copolymer.

Cyclic Voltammetry

Cyclic voltammetry (C-V) was employed to investigate the redox behavior of the resulting conjugated polymers and to estimate their HOMO and LUMO energy levels. TAZ-CAR-PPV or TAZ-BCAR-PPV film dip-coated on a Pt electrode was scanned positively and negatively separately in 0.1 mol/L Bu_4NClO_4 in anhydrous acetonitrile. Figure 4 depicts the C-V spectra of TAZ-CAR-PPV and TAZ-BCAR-PPV, respectively. Under the anodic scan, TAZ-BCAR-PPV exhibits two-electron-transfer reversible *p*-doping and dedoping processes. The anodic peaks appear at 1.15 and 1.49 V (versus Ag/AgCl) with the corresponding cathodic peaks appear at 0.67 and 1.30 V (versus Ag/AgCl), respectively. The onset of *p*-doping is determined to be 0.82 V. Under negative scan, an irreversible redox curve was observed. The onset of *n*-doping is determined to be -1.88 V . The reduction potential is comparable to that of 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) (1.95 versus SCE)^[18]. This can be attributed to the introduction of electron-withdrawing triazole group. The energy levels of TAZ-BCAR-PPV were calculated using the ferrocene (FOC) value of -4.8 eV as the standard. The onset potentials of the oxidation and reduction were determined to be 0.38 eV and -2.32 eV versus FOC ($E_{\text{FOC}} = 0.44$ eV versus Ag/AgCl). Therefore, the HOMO, LUMO and energy levels and the band gap (E_g) were estimated to be -5.18 , -2.48 and 2.70 eV, respectively. The band gap obtained from the electrochemical measurement is quite close to the result determined by the absorption spectrum of the TAZ-BCAR-PPV ($\lambda_{\text{onset}} = 455$ nm, $E_g = 2.72$ eV). However, TAZ-CAR-PPV exhibits the irreversible redox process, as shown in Fig. 4. Its HOMO, LUMO and band gap were determined to be -5.26 , -2.55 and 2.71 eV, respectively.

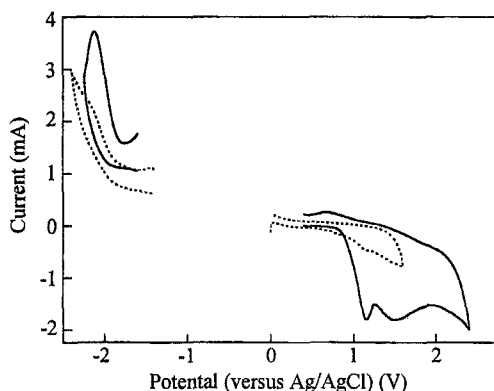


Fig. 4 Cyclic voltammograms of TAZ-CAR-PPV (----) and TAZ-BCAR-PPV (—) at a scanning rate of 50 mV/s versus Ag/AgCl

CONCLUSIONS

In summary, we have synthesized and characterized two new bipolar PPV-based conjugated copolymers containing triazole and carbazole units (TAZ-CAR-PPV) and carbazole dimer (TAZ-BCAR-PPV). The emissive light of TAZ-CAR-PPV and TAZ-BCAR-PPV films shows blue colour with the maximum PL wavelength of 460 and 480 nm, respectively. These polymers have well-defined structures and exhibit good thermal stability. The incorporation of the triazole moiety into the polymer backbone significantly enhances the thermal stability of the resulting polymers. Moreover, the triazole unit is also an effective π -conjugation interrupter and can act as the rigid spacer in determining the emission colour of the copolymer. The introduction of the carbazole moiety or carbazole dimer into the polymer backbone determines the effective conjugation length and the photoluminescence wavelength of the copolymer. Our research on charge transporting properties and LED devices is on-going.

Acknowledgement The authors would like to thank Prof. Jing-ping Zhang for useful discussions.

REFERENCES

- 1 Burroughes, J.H., Bradley, D.D.C., Brown, A.R., Marks, R.N., Mackay, K., Friend, R.H., Burn, P.L. and Holmes, A.B., *Nature*, 1990, 347: 539
- 2 Son, S., Dodabalapur, A., Lovinger, A.J. and Galvin, M. E., *Science*, 1995, 269: 376
- 3 Greenham, N.C., Moratti, S.C., Bradley, D.D.C., Friend, R.H. and Holmes, A.B., *Nature*, 1993, 365: 628
- 4 Tamoto, N., Adachi, C. and Nagai, K., *Chem. Materl.*, 1997, 9: 1077
- 5 Kido, J., Harada, G. and Nagai, K., *Chem. Lett.*, 1996, 161
- 6 Peng, Z., Bao, Z. and Galvin, M. E., *Adv. Materl.*, 1998, 10: 680
- 7 Song, S.Y., Jang, M. S., Shim, H. K., Hwang, D.H. and Zyung, T., *Macromolecules*, 1999, 32: 1482
- 8 Friend, R.H., Gymer, R.W., Holmes, A.B., Burroughes, J.H., Marks, R.N., Taliani, C., Bradley, D.D.C., Santos, D.A.D., Bredas, J.L., Logtdlund, M. and Salaneck, W.R., *Nature*, 1999, 397: 121
- 9 Heeger, A.J., *Solid State Commun.*, 1998, 107: 673
- 10 Grice, A. W., Tajbakhsh, A., Burn, P.L. and Bradley, D.D.C., *Adv. Materl.*, 1997, 9: 1174
- 11 Ahn, T., Jang, M.S., Shim, H.K., Hwang, D.H. and Zyung, T., *Macromolecules*, 1999, 32: 3279
- 12 Strukelj, M., Miller, T.M., Papadimitrakopoulos, F. and Son, S., *J. Am. Chem. Soc.*, 1995, 117: 11976
- 13 Strukelj, M., Papadimitrakopoulos, F., Miller, T.M., Rothberg, L.J.A. and Chandross, E., *Science*, 1995, 267: 1969
- 14 Kido, J., Ohtaki, C., Hongawa, K., Okuyama, K. and Nagai, K., *Jpn. J. Appl. Phys.*, 1993, 32: L917
- 15 Carter, K.R., Miller, R.D. and Hedrick, J.L., *Macromolecules*, 1993, 26: 2209
- 16 Boucard, V., Benazzi, T., Ades, D., Sauvet, G. and Siove, A., *Polymer*, 1997, 38: 3697
- 17 For TAZ-CAR-PPV, Anal. Calcd: for (C₄₄H₄₀N₄): C 84.62, H 6.41, N 8.97; found: C 84.11, H 6.88, N 9.01. For TAZ-BCAR-PPV, Anal. Calcd: for (C₆₄H₆₃N₅): C 85.24, H 6.99, N 7.77; found: C 84.46, H 6.50, N 8.84
- 18 Bomero, D.B., Nuesch, F., Benazzi, T., Ades, D., Siove, A. and Zuppiroli, L., *Adv. Materl.*, 1997, 9: 1158
- 19 Janietz, S. and Wedel, A., *Adv. Materl.*, 1997, 9: 403