# Effect of Conjugated Core Building Block Dibenzo[a,c]phenazine Unit on $\pi$ -Conjugated Electrochromic Polymers: Red-Shifted Absorption

ELIF KOSE UNVER,<sup>1</sup> SIMGE TARKUC,<sup>1</sup> YASEMIN ARSLAN UDUM,<sup>2</sup> CIHANGIR TANYELI,<sup>1</sup> LEVENT TOPPARE<sup>1,\*</sup>

<sup>1</sup>Department of Chemistry, Middle East Technical University, Ankara 06531, Turkey

<sup>2</sup>Department of Advanced Technologies, Institute of Science and Technology, Gazi University, Ankara 06570, Turkey

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**ABSTRACT:** A comparative investigation was undertaken for the electrosynthesis and electrochemical properties of three different electroactive polymers having a conjugated core building block, dibenzo[a,c]phenazine. A series of monomers has been synthesized as regards to thiophene based units; thiophene, 3-hexyl thiophene, and 3,4-ethylenedioxythiophene. The effects of different donor substituents on the polymers' electrochemical properties were examined by cyclic voltammetry. Introducing highly electron-donating (ethylene dioxy) group to the monomer enables solubility while also lowering the oxidation potential. The planarity of the monomer unit enhances  $\pi$ -stacking and consequently lowering the  $E_g$  from 2.4 eV (PHTP) to 1.7 (PTBP). Cyclic voltammetry and spectroelectrochemical

measurements revealed that 2,7-bis(4-hexylthiophen-2-yl)dibenzo[a,c]phenazine (HTP) and 2,7-bis(2,3-dihydrothieno[3,4b][1,4]dioxin-5-yl)dibenzo[a,c]phenazine (TBP) possessed electrochromic behavior. The colorimetry analysis revealed that while PTBP have a color change from red to blue, PHTP has yellow color at neutral state and blue color at oxidized state. Hence the presence of the phenazine derivative as the acceptor unit causes a red shift in the polymers' absorption to have a blue color. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 1714–1720, 2010

**KEYWORDS**: conducting polymers; conjugated materials; dibenzophenazine; electrochemistry; electrochromism; redox polymers

**INTRODUCTION** The design and synthesis of new  $\pi$ -conjugated polymers attract great attention in the field of organic semiconductors due to their potential applications in electrochromic displays,<sup>1</sup> light emitting diodes (LEDs),<sup>2</sup> and photovoltaic devices.<sup>3–5</sup> The color changes induced in  $\pi$ -conjugated polymers by the electrochemical doping/dedoping process offer a broad set of new materials for electrochromic applications.<sup>6,7</sup> The major advantage of these organic based materials is that their electrochromic properties can be tuned through chemical structure modification.<sup>8,9</sup> Besides structural variations on the monomer repeat via substitution of functional groups, the design of new precursor structures allows a significant reduction of the band gap energy  $(E_{g})$ .<sup>10,11</sup> In designing low band gap systems, the methodologies that can be used to synthesize polymers with  $E_{g}$ less than 2 eV are controlling bond-alternation, creating highly planar systems, inducing order by interchain effects, resonance effects along the polymer backbone, and using donor-acceptor effects.<sup>12-14</sup> In more planar systems, better orbital overlap leads to a lowering of the band gap. The reduction in  $E_{\rm g}$  has been ascribed to an increased contribution of the quinoid structure, brought about by fused benzene ring.<sup>15</sup> Due to the deviation from the planarity and the interring twisting on polymer, new electronic states are formed resulting in shifts in the optical absorptions to longer wavelength. These polymers are generally colored both in the neutral, nonconducting, and doped, conducting states. The oxidatively doped conducting polymers

are generally even more highly colored and opaque than their neutral counterparts.

In this study, a new family of donor-acceptor-donor polymer with phenazine moieties as the core building block was synthesized (Scheme 1). The reason behind the choice of this approach is that a fully conjugated phenazine backbone allows planarity while donor moieties tune the solubility and electrochromic properties of the resulting polymers.

## **EXPERIMENTAL**

#### Materials

Dichloromethane (DCM), ethanol, *N*-bromosuccinimide (NBS), dimethylsulfoxide (DMSO), phenanthrene-9,10-dione, diaminobenzene, dichlorobis(triphenylphosphine)palladium (II), and para-toluene sulfonic acid (PTSA) were purchased from Sigma-Aldrich. Chloroform (CHCl<sub>3</sub>) concentrated sulfuric acid and silica gel (70–230 mesh) were purchased from Merck, while tetrahydrofuran (THF) was purchased from Fisher Scientific U.K. Limited. Tributylstannane compounds were synthesized according to previously described methods. THF was dried and distilled over benzophenone-sodium under nitrogen before use.

#### Instrument

 $^{1}\mathrm{H}$  NMR and  $^{13}\mathrm{C}$  NMR spectra were recorded with a Bruker Spectrospin Avance DPX-400 Spectrometer at 400 MHz and

Correspondence to: L. Toppare (E-mail: toppare@metu.edu.tr)

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SCHEME 1 Chemical structures of TTP, HTP, and TBP.

TBP

chemical shifts ( $\delta$ ) were determined relative to tetramethylsilane as the internal standard. Electropolymerization was performed with a Voltalab 50 potentiostat in a three-electrode cell consisting of indium tin oxide doped glass slide (ITO) as the working electrode, platinum wire as the counter electrode, and Ag wire as the pseudo-reference electrode. Varian Cary 5000 spectrophotometer was used to perform the spectroelectrochemical studies of the polymers. Colorimetry measurements were performed via Minolta CS-100 spectrophotometer. HRMS data was acquired at the Center for Genomics, University at Albany, Rensselaer, NY on QSTAR XL and ESI -Q-TOF II (Waters, Milford, MA, USA). Samples were dissolved in 100  $\mu$ L CH<sub>2</sub>Cl<sub>2</sub>.

## **Synthesis**

## 2,7-Dibromophenanthrene-9,10-dione: (2)

NBS (1.795 g, 10.09 mmol) was added to a well stirred solution of phenanthrene-9,10-dione 1 (1 g, 4.80 mmol) in 98% H<sub>2</sub>SO<sub>4</sub> and stirred at room temperature for 3 h. The mixture was poured on crushed ice. The orange product was filtered off and washed with cold water. It was recrystallized in DMSO.<sup>16-18</sup> (1.31 g, 75%) M.P. 326.8 °C (by DSC). <sup>1</sup>H NMR (400MHz d<sub>6</sub>-DMSO):  $\delta$  (ppm) 8.25 (d, 2H, J = 8.4 Hz), 8.09 (d, 2H, *J* = 1.9 Hz), 7.96 (dd, 2H, *J* = 8.4, 1.9 Hz).

## 2,7-Dibromodibenzo[a,c]phenazine: (3)

2,7-Dibromophenanthrene-9,10-dione (300 mg, 0.82 mmol) and diaminobenzene (88.64 mg, 0.82 mmol) were dissolved in ethanol. Catalytic amount PTSA was added in the solution. The mixture was refluxed for 5 h. A yellow colored cloudy mixture was observed. Filtration of the reaction mixture followed by washing with ethanol afforded the product as an vellow solid (310 mg, 86%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ (ppm) 9.46 (d, 2H, I = 2.2 Hz), 8.29 (m, 4 H), 7.83 (m, 4H) <sup>13</sup>C NMR (100 MHz, CDCI<sub>3</sub>):  $\delta$  (ppm) 142.7, 133.7, 132.2, 130.8, 130.4, 129.8, 129.4, 124.9, 123.2, 100.3.

## 2,7-Di(thiophen-2-yl)dibenzo[a,c]phenazine: (4, TTP)

2,7-Dibromodibenzo[a,c]phenazine (100 mg, 0.23 mmol) and tributyl(thiophen-2-yl)stannane<sup>19</sup> (343.33 mg, 0.92 mmol) were dissolved in anhydrous THF (150 mL). The solution

was purged with argon for 30 min and dichlorobis(triphenyl phosphine)palladium(II) (40 mg, 0.057 mmol) was added at room temperature. The mixture was refluxed for 15 h under argon atmosphere. A yellow solid was observed in the reaction medium. Solvent was filtered to remove the solvent. The solid was washed with dichloromethane to obtain gold like yellow solid (73 mg, 71%).

<sup>1</sup>H NMR (400 MHz, d6-DMF) (Fig. 1):  $\delta$  (ppm) 9.83 (d, 2H, J = 1.6 Hz), 9.10 (d, 2H, J = 8.3 Hz), 8.64 (dd, 2H, J = 6.4, 3.2 Hz), 8.47 (d, 2H, J = 8.3 Hz), 8.26 (dd, 2 H, J = 6.4, 3.2 Hz), 8.06 (d, 2H, J = 3.3 Hz), 7.93 (d, 2H, J = 5.0 Hz), 7.50 (t, 2H, I = 5.0, 3.3 Hz) HRMS m/z calcd for ( $C_{28}H_{16}N_2S_2$ ) 445.0833; found 445.0814 [M+H]+.

## 2,7-Bis(4-hexylthiophen-2-yl)dibenzo[a,c] phenazine: (5, HTP)

2,7-Dibromodibenzo[a,c]phenazine (100 mg, 0.23 mmol), and tributyl(4-hexylthiophen-2-yl)stannane<sup>20</sup> (418 mg, 0.92 mmol) were dissolved in anhydrous THF (150 mL), the solution was purged with argon for 30 min and dichlorobis(triphenyl phosphine)palladium(II) (40 mg, 0.057 mmol) was added at room temperature. The mixture was refluxed for 14 h under argon atmosphere. Solvent was evaporated under vacuum and the crude product was purified by column chromatography over silica gel, eluting with 1:2 (chloroform: hexane) to give a yellow solid (96 mg, 64%).

<sup>1</sup>H NMR (400 MHz, CDCI<sub>3</sub>) (Fig. 2):  $\delta$  (ppm) 9.44 (s, 2H), 8.35 (d, 2H, J = 8.4 Hz), 8.29 (dd, 2H, J = 6.4, 3.3 Hz), 7.87 (d, 2H, I = 8.4), 7.79 (dd, 2H, I = 6.4, 3.3 Hz), 7.40 (s, 2H),6.91 (s, 2H), 2.63 (t, 4H, J = 7.6 Hz), 1.66 (m, 4H), 1.32 (m, 12 H), 0.85 (t, 6H, J = 6.8 Hz), <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ (ppm) 144.9, 143.8, 142.6, 142.5, 134.4, 130.9, 130.8, 130.1, 129.8, 127.9, 125.6, 123.7, 122.9, 120.5, 32.0, 31.0, 30.8, 29.4, 22.9, 14.4.

## 2,7-Bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl) dibenzo[a,c]phenazine: (6, TBP)

2,7-Dibromodibenzo[a,c]phenazine (100 mg, 0.23 mmol) and tributyl(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)stannane<sup>21</sup>



**FIGURE 1** <sup>1</sup>H NMR spectrum of 2,7-di(thiophen-2-yl)dibenzo[a,c]phenazine (TTP). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

(396.7 mg, 0.92 mmol) were dissolved in anhydrous THF (150 mL), the solution was purged with argon for 30 min and dichlorobis(triphenyl phosphine)palladium(II) (40 mg, 0.057 mmol) was added at room temperature. The mixture was refluxed for 12 h under argon atmosphere. Solvent was evaporated under vacuum and the crude product was purified by column chromatography over silica gel, eluting with 2:1 (chloroform:hexane) to give a brownish orange solid (85 mg, 66 %).

<sup>1</sup>H NMR (400 MHz, CDCI<sub>3</sub>) (Fig. 3):  $\delta$  (ppm) 9.59 (d, 2H, J = 2.0 Hz), 8.43 (d, 2H, J = 8.5 Hz), 8.31 (dd, 2H, J = 6.5,

3.3 Hz), 8.11 (dd, 2H, J = 8.5, 2.0 Hz), 7.79 (dd, 2H, J = 6.5, 3.3 Hz), 6.36 (s, 2H), 4.39 (m, 4H), 4.27 (m, 4H) <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 141.4, 141.2, 141.0, 137.8, 131.6, 129.3, 129.0, 128.5, 128.4, 126.9, 122.1, 121.8, 116.1, 97.3, 63.8, 63.4. HRMS *m*/*z* calcd for (C<sub>32</sub>H<sub>20</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub>) 561.0943; found 561.0961 [M+H]+ (Fig. 4).

## **RESULTS AND DISCUSSION**

### Synthesis

Scheme 2 shows the way, the monomers were prepared using phenanthrene-9,10-quinone as the starting material.



FIGURE 2 <sup>1</sup>H NMR spectrum of 2,7-bis(4-hexylthiophen-2-yl)dibenzo[a,c]phenazine (HTP). [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]



FIGURE 3 <sup>1</sup>H NMR spectrum of 2,7-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)dibenzo[a,c]phenazine (TBP). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

According to a method in literature,<sup>16</sup> phenanthrene-9,10quinone was brominated by treatment with NBS in concentrated  $H_2SO_4$ . The condensation reaction takes place between 2,7-dibromophenanthrene-9,10-quinone 5 with the 1,2-di-



FIGURE 4 HRMS data for (a) TTP (b) TBP.

aminobenzene gave 2,7-dibromodibenzo[a,c]phenazine in good yield (86%). Stannylation of 3-hexyl thiophene, ethylenedioxythiophene (EDOT), and thiophene was achieved by addition of equimolar strong base, *n*-BuLi followed by addition of Bu<sub>3</sub>SnCl. Finally, Stille coupling,<sup>22,23</sup> was used to attach donor moieties to the acceptor phenazine unit to give the desired monomers in satisfactory yields (64–71%).

## Electrochemistry

Electroactivities of monomers were investigated using cyclic voltammetry. Analysis of TTP showed poor film-forming ability



SCHEME 2 Synthetic route to monomers.



FIGURE 5 Repeated potential scan electropolymerization of (a) TBP and (b) HTP at 100 mV/s in 0.1 M TBAPF<sub>6</sub>/DCM on the ITO electrode.

in dichloromethane (DCM), acetonitrile (ACN), benzonitrile, and tetrahydrofuran (THF). Hence, this polymer was not good enough to produce films with a sufficient quality for electrochromic studies. Figure 5 shows the cyclic voltammograms corresponding to the potentiodynamic polymerization of TBP and HTP by application of consecutive potential scans. In each case, the first cycle shows an irreversible anodic wave corresponding to the oxidation of the monomer. Subsequent cycling leads to a new redox system associated with the oxidation and reduction of the polymer deposited on the electrode surface.

Cyclic voltammograms of TBP and HTP were obtained in dichloromethane (DCM) containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) with a scan rate of 100 mV/s. Electropolymerization of TBP was performed using multiple scan voltammetry between +0.4 V and +1.3 V on ITO electrode. TBP monomer started to get oxidized at +1.1 V vs the Ag wire pseudo-reference electrode (0.35 V vs SCE) during the first anodic sweep. The redox behavior of HTP was studied by scanning the potential between +0.3 V and +1.4 V. For HTP monomer, the onset of oxidation started at a slightly higher potential (+1.2 V vs the Ag wire pseudo-reference electrode). As expected, the oxidation of HTP was observed at higher potential than that of TBP due to the difference in electronic nature of the external moieties (3-hexyl thiophene and EDOT). Upon repeated scanning the increasing current response of the polymer redox process illustrates that electrochemical polymerization is proceeding on the electrode surface to form an electroactive polymer film. During the anodic scans polymer oxidations were observed at +1.0 V for PTBP and +1.17 V for PHTP. Reduction peaks of the polymers were at +0.77 V for PTBP and +0.93 V for PHTP vs the same reference electrode (Table 1).

Cyclic voltammograms were obtained at different scan rates to test the mass transfer on the electrode (Fig. 6). Anodic and cathodic peak currents reveal a linear relationship as a function of scan rate for both polymers, which proves that the films were well-adhered and electroactive. The linear increase of the current upon incrementing the scan also indicates that the electrochemical processes are not diffusion limited and are quasi-reversible even at high scan rates.

## **Spectroelectrochemical Studies**

To probe the electronic structure of the polymers and examine the optical changes upon doping, spectroelectrochemical analyses were performed. For that matter, polymer films were deposited on ITO-coated glass slides from  $1.10^{-2}$  M monomer solutions in 0.1 M TBAPF<sub>6</sub>/DCM. The optical changes were investigated by UV-Vis-NIR spectroscopy in a monomer-free TBAPF<sub>6</sub>/DCM solution via applying different voltages. Fig. 7 reveals spectroelectrochemistry and corresponding colors of PTBP and PHTP at their reduced and oxidized states.

Oxidation of an electrochromic material produces radical cations (polarons) and further oxidation produces dications (bipolarons), allowing new electronic transition thereby changing absorption spectra. As seen from the spectroelectrochemical series, upon stepwise oxidation of all the polymers, the absorption of  $\pi$ - $\pi^*$  transitions decreased while those of the polaron and bipolaron peaks increased. The absorption assigned to  $\pi$ - $\pi^*$  transition for PTBP is at 580 nm. The band gap of the polymer was calculated as 1.7 eV from the onset of the  $\pi$ - $\pi^*$  transition. As the potential applied to the film increases, the broad absorption peaks at about 580 and 1230 nm, which correspond to polaron and bipolaron species, respectively, also increase. Presence of alkyl chains at the  $\beta$ -position of thiophene ring has influence on the electronic structure of the  $\pi$ -conjugated system where

**TABLE 1** CV Data and Calculated HOMO and LUMO Energies for the Polymers

Oxidation Potential (V)		Bandgap (eV)	Energy Level (eV)	
Eox	E <sub>onset,ox</sub>	$E_{g}^{op}$	НОМО	LUMO
1.0	-0.45	1.7	-4.35	-2.65
1.17	0.58	2.4	-5.33	-2.93
	Oxi Pote <i>E</i> <sub>ox</sub> 1.0 1.17	Oxidation Potential (V)EoxEonset,ox1.0-0.451.170.58	Oxidation Potential (V)Bandgap (eV) $E_{ox}$ $E_{onset,ox}$ $E_g^{op}$ 1.0-0.451.71.170.582.4	$\begin{array}{c} \begin{array}{c} Oxidation \\ Potential (V) \\ \hline E_{ox} \\ 1.0 \\ 1.17 \end{array} & \begin{array}{c} E_{onset,ox} \\ e_{g}^{op} \\ 1.7 \\ 2.4 \\ 2.4 \end{array} & \begin{array}{c} E_{nergy} \\ e_{g}^{op} \\ \hline HOMO \\ -4.35 \\ -5.33 \end{array}$



FIGURE 6 Cyclic voltammograms of (a) PTBP and (b) PHTP in 0.1 M TBAPF<sub>6</sub>/DCM at scan rates of 100, 150,200, 250, and 300 mV/s.

the onset of the  $\pi$ - $\pi$ <sup>\*</sup> transition shifts to shorter wavelength. PHTP exhibits a larger  $E_{\rm g}$  value (2.4 eV) than PTBP.

The different structures of the polymers due to the differences in donor moiety affect not only the monomer oxidation and the polymer redox couple potentials but also the maximum absorption wavelengths of the corresponding transition. The introduction of alkyl substituents on polymer causes steric hindrance, resulting in less order and less conjugation by the blue shift in absorption spectra and the increase in polymer' band gap.

The color changes were further investigated by colorimetry using the CIE 1931 Yxy color space to define color precisely. PTBP becomes red (Y: 176; x: 0.395; y: 0.337) in the neutral state, while its oxidized state is blue (Y: 204; x: 0.251; y:

0.273). PHTP film changed from a yellow neutral state (Y: 821; x: 0.352; y: 0.386) to a blue oxidized state (Y: 538; x: 0.263; y: 0.309).

## **Electrochromic Switching Studies**

The stability and switching time upon electrochromic switching of the polymer films between their neutral and oxidized forms were monitored in the visible and NIR regions. The switching time, which is defined as the time required for 95% of the full change in absorption was estimated by applying a square-wave potential coupled with optical spectroscopy. In this experiment, the potential was set at an initial potential for a given period of time (5s), and was stepped to a second potential for the same period of time (5s) before being switched back to the initial potential. During the experiment, the % transmittance (%T) at different wavelengths was measured with a UV-Vis-NIR spectrophotometer.

To allow a comparison of the polymers, the results of these switching studies for PTBP and PHTP are shown in Figure 8. PTBP revealed impressing switching times of 0.4 s at 470 nm and 0.6 s at 580 nm while switching the applied potential between +0.4 V and +1.3 V. This switching ability persists for over 3000 cycles. The percent transmittance between neutral and oxidized states was found to be 22% for 470 nm and 8% for 580 nm. At 1230 nm PTBP films show an optical contrast of 50% with a fast switching time



FIGURE 7 p-Doping spectroelectrochemistry of (a) PTBP and (b) PHTP films on an ITO-coated glass slide in monomer-free, 0.1 M TBAPF<sub>6</sub>/DCM electrolyte-solvent couple at applied potentials.



FIGURE 8 (a) Electrochromic switching and optical absorption change monitored at 470, 580, and 1230 nm for PTBP in 0.1 M TBAPF<sub>6</sub>/DCM. (b) Electrochromic switching and optical absorption change monitored at 380, 610, and 1400 nm for PHTP in 0.1 M TBAPF<sub>6</sub>/DCM. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

of approximately 1 s. PHTP was switched between +0.3 V and +1.4 V. The optical contrasts were found to be 17% at 380 nm and 38% at 610 nm. The switching times were calculated as 2.5 s at 380 nm and 1.8 s at 610 nm. About 1 s was required for PHTP films to accomplish an optical contrast of 54% at 1400 nm. The switching ability of PHTP lasts for only a little over 400 cycles.

#### **CONCLUSIONS**

A series of monomers differing by the electron-donating groups along the backbone have been synthesized and characterized. Introduction of highly electron-donating (ethylene dioxy unit) group to the monomer not only leads to good solubility, but also a lower oxidation potential. The planarity of the monomer unit allows for a better packing of the monomer chains, thus enhancing  $\pi$ -stacking and consequently lowering the  $E_{\rm g}$  from 2.4 eV (PHTP) to 1.7 (PTBP).

The optical contrasts for PTBP were calculated as 22% at 470 nm, 8% at 580 nm, and 50% at 1230 nm. PHTP

achieves 17% at 380 nm, 38% at 610 nm and 54% at 1400 nm.

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### **REFERENCES AND NOTES**

1 Sonmez, G.; Meng, H.; Zhang, Q.; Wudl, F. Adv Funct Mater 2003, 13, 726–731.

2 Kraft, A.; Grimsdale, A. C.; Holmes, A. B. Angew Chem Int Ed Engl 1998, 37, 403–428.

**3** Huynh, W. U.; Dittmer, J. J.; Alivisatos, A. P. Science 2002, 295, 2425–2427.

4 Liang, C. W.; Su, W. F.; Wang, L. Appl Phys Lett 2009, 95, 133303–133305.

**5** Lin, Y. Y.; Chu, T. H.; Li, S. S.; Chuang, C. H.; Chang, C. H.; Su, W. F.; Chang, C. P.; Chu, M. W.; Chen, C. W. J Am Chem Soc 2009, 131, 3644–3649.

6 Udum, Y. A.; Yildiz, E.; Gunbas, G.; Toppare, L. J Polym Sci Part A: Polym Chem 2008, 46, 3723–3731.

7 Rosseinsky, D. R.; Mortimer, R. J. Adv Mater 2001, 13, 783–793.

8 Roncali, J. Chem Rev 1992, 92, 711-738.

**9** Durmus, A.; Gunbas, G. E.; Toppare, L. Chem Mater 2007, 19, 6247–6251.

**10** Zoombelt, A. P.; Gilot, J.; Wienk, M. M.; Janssen, R. A. J. Chem Mater 2009, 21, 1663–1669.

**11** Mishra, S. P.; Palai, A. K.; Srivastava, R.; Kamalasanan, M. N.; Patri, M. J Polym Sci Part A: Polym Chem 2009, 47, 6514–6525.

12 Roncali, J. Chem Rev 1997, 97, 173-205.

13 Salzner, U. J Phys Chem B 2002, 106, 9214-9220.

14 Berlin, A.; Zotti, G.; Zecchin, S.; Schiavon, G.; Vercelli, B.; Zanelli, A. Chem Mater 2004, 16, 3667–3676.

15 McCullough, R. D. Adv Mater 1998, 10, 93-116.

**16** Hanif, M.; Lu, P.; Li, M.; Zheng, Y.; Xie, Z.; Ma, Y.; Li, D.; Li, J. Polym Int 2007, 56, 1507–1513.

17 Dewhurst, F.; Shah, P. K. J. J Chem Soc 1969, 1503– 1504.

**18** He, B.; Tian, H.; Geng, Y.; Wang, F.; Muellen, K. Org Lett 2008, 10, 773–776.

**19** Xia, Y.; Luo, J.; Deng, X.; Li, X.; Li, D.; Zhu, X.; Yang, W.; Cao, Y. Macromol Chem Phys 2006, 207, 511–520.

**20** Hou, Q.; Zhou, Q.; Zhang, Y.; Yang, W.; Yang, R.; Cao, Y. Macromolecules 2004, 37, 6299–6305.

**21** Zhu, S. S.; Swager, T. M. J Am Chem Soc 1997, 119, 12568–12577.

22 Milstein, D.; Stille, J. K. J Am Chem Soc 1978, 100, 3636–3638.

23 Stille, J. K. Angew Chem Int Ed Engl 1986, 25, 508-524.