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Synthesis and optical properties of two novel stilbene derivatives containing 1,3,4-oxadiazole moiety

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ABSTRACT

Two novel stilbene derivatives containing 1,3,4-oxadiazole moiety were synthesized and characterized by elemental analyses, ^{1}H NMR, MS. The photophysical processes of the title compounds were investigated by UV–vis absorption and fluorescence emission spectra in different solutions. The fluorescence quantum yield (Φ) of **1a** and **1b** in THF is 0.65 and 0.69, respectively. The influence of the solution on the fluorescence intensities was also discussed. Under ultraviolet light excitation, the two compounds exhibit strong blue fluorescence emission. They may serve as potential applications in organic electroluminescent materials.

1. Introduction

It is well known that stilbene derivatives have considerable biological and medical activities, such as anti-microbial and insecticidal effects, vasodilation action, and insect baculovirus synergists [1–5]. In addition, interesting features of the stilbene derivatives are their effects on light and witness applications in main chain liquid crystalline polymers [6,7], PPV-type electroluminescent copolymer [8], optical brighteners and photochemically crosslinkable polymers. The stilbene skeleton could be an excellent choice for a central chromophore with which to construct new photoresponsive materials [9]. Moreover, stilbene derivatives show distinctive blue fluorescence emission properties to be used in organic electroluminescent (EL) materials [10,11]. However, there still remain many important and fundamental challenges. A blue light-emitting material with high efficiency deep blue color, better thermal stability and long operational lifetime is till in demand, especially the emission of the light at the blue end of the visible spectrum, which is crucial for many applications [12]. To obtain stable EL devices and high fluorescence quantum yield, a well-balanced injection of positive (hole) and negative (electron) charge carrier into an emitting layer is considered to be prerequisite for high luminous efficiency. Recently considerable research efforts have been carried out to enhance performance suitable for practical use [13,14]. Many 1,3,4-oxadiazole derivatives with good hole-transporting capabilities, durability and thermal stability, especially high fluorescence quantum yields, have actually been used as electron-injection materials to improve the balance of charge carrier and to increase the proton/electron quantum efficiency [15,16]. Furthermore, oxadiazole rings can increase the degree of conjugation of the stilbene derivative. In this paper, we report the synthesis of a four-step synthesis of stilbene derivatives containing 1,3,4-oxadiazole moiety, which may serve as potential intramolecular charge transfer compounds, the requisite 2,5-di-*p*-tolyl-1,3,4-oxadiazole framework is available via the direct coupling of *p*-toluic acid with hydrazine hydrate promoted by polyphosphoric acid. The photophysical processes of the title compounds are investigated by UV–vis absorption and fluorescence emission spectra in chloroform, THF, acetone and DMF. The results show the two compounds exhibit strong blue fluorescence emission, which may serve as potential application in organic electroluminescent materials. The synthetic route is outlined in Scheme 1.

2. Experimental

2.1. Instrumentation

Melting points were determined using RY-1 melting point apparatus and were uncorrected. ^{1}H NMR spectra were recorded in $CDCl_3$ on a Bruker AVANCE-600 MHz NMR spectrometer using TMS as internal standard. Mass spectra were obtained with a HPLC/MS LCQDECA spectrometer (APCI). Elemental analyses were performed on a Vario EL III CHN elemental analyzer. UV–vis absorption spectra were recorded on a Hitachi UV-3010 spectrophotometer. Fluorescence spectra were obtained on a Hitachi

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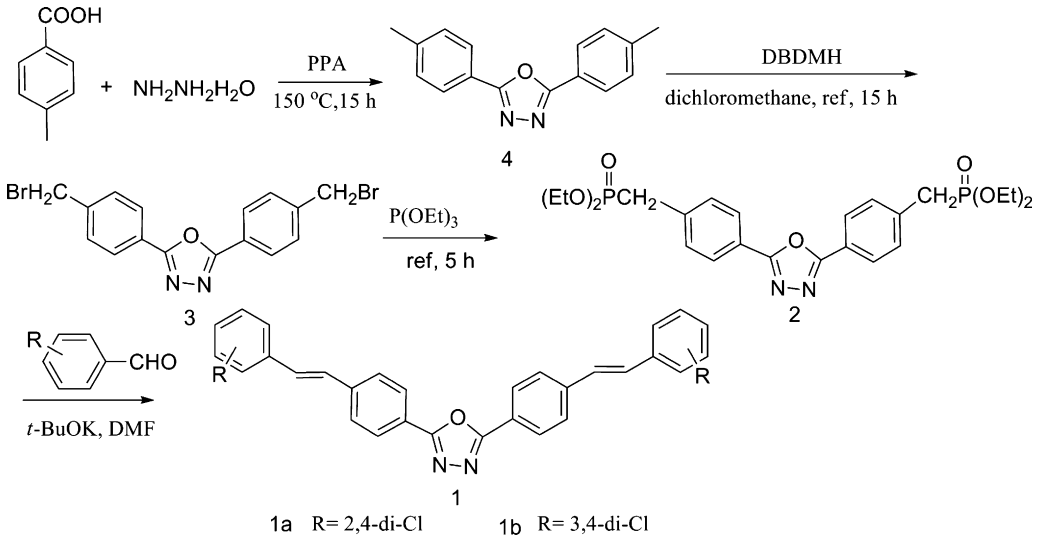

Scheme 1. The synthetic route of the title compounds.

F-4500 spectrophotometer at room temperature. The fluorescence quantum yields $\Phi_x = (A_s \times F_x \times n_x^2 \times \Phi_s)/(A_x \times F_s \times n_s^2)$ where A is the absorbance at the excitation wavelength, F the area under the fluorescence curve and n the refraction index. Subscripts s and x refer to the standard and to the sample of unknown quantum yield, respectively. Rhodamine B in ethanol ($\Phi = 0.89$) was taken as the standard [17].

2.2. Synthesis

2.2.1. Synthesis of 2,5-di-p-tolyl-1,3,4-oxadiazole (4)

p-Toluic acid (17 g, 125 mmol) and 80% hydrazine hydrate (4 mL, 66 mmol) were added to 60 mL of stirred phosphoric acid, respectively, the reaction proceeded at 150 °C for 15 h until the disappearance of the starting material by TLC. The cool mixture was poured into cold water, neutralized by 5% Na_2CO_3 and filtered, the residue was recrystallized from $CHCl_3$/methanol giving 9.4 g of compound **4** as white crystals, yield 60%, m.p. 176–177 °C; ^{1}H NMR ($CDCl_3$): δ 2.43 (s, 6H, CH_3), 7.32 (d, J = 8.4 Hz, 4H, C_6H_4 3,5-H), 8.01 (d, J = 8.4 Hz, 4H, C_6H_4 2,6-H); APCI MS: m/z, 251 (M+1, 100), 252 (M+2, 18).

2.2.2. Synthesis of 2,5-bis(4-(bromomethyl)phenyl)-1,3,4-oxadiazole (3)

To a stirred solution of **4** (5 g, 20 mmol) in carbon dichloride (70 mL) was added DBDMH (4 g, 20 mmol), the reaction proceeded with refluxing for 15 h and then the excess solvent was removed. The resulting mixture was filtered, washed with ethanol. The residue was recrystallized from THF/ethanol giving 6 g of compound **3** as white crystals, yield 75%, m.p. 227–228 °C; ^{1}H NMR ($CDCl_3$): δ 4.55 (s, 4H, CH_2Br), 7.57 (d, J = 8.4 Hz, 4H, C_6H_4 3,5-H), 8.13 (d, J = 8.4 Hz, 4H, C_6H_4 2,6-H); APCI MS: m/z, 409 (M+1, 100).

2.2.3. Synthesis of diethyl 4-(5-(4-(diethoxyphosphino)methyl)phenyl)-1,3,4-oxadiazol-2-yl)-benzyl-phosphonate (2)

A mixture of compound **3** (5 g, 14.7 mmol) and triethyl phosphite (13 mL, 76.6 mmol) was refluxed for 5 h. The excess triethyl phosphate was evaporated under reduced pressure, then filtered by addition of hexane. The residue was recrystallized from THF/hexane giving 6.2 g of compound **2**, yield 80%, m.p. 111–112 °C; ^{1}H NMR ($CDCl_3$): δ 1.27 (t, J = 7.2 Hz, 12H, CH_3), 3.43 (d, J = 22.2 Hz, 4H, CH_2), 4.02–4.08 (m, 8H, OCH_2), 7.49 (dd, J = 2.4 Hz, J = 8.4 Hz, 4H, C_6H_4 3,5-H), 8.09 (d, J = 8.4 Hz, 4H, C_6H_4 2,6-H).

2.2.4. Typical procedure for the synthesis of compounds 1

To a stirred solution of aromatic aldehydes (3.4 mmol) and the intermediate **2** (0.9 g, 1.7 mmol) in anhydrous N, *N*-dimethylformamide (15 mL) under nitrogen atmosphere was added dropwise a solution of *t*-BuOK (2 g, 3%) in ethanol. The reaction proceeded at room temperature overnight. Then the resulting mixture was filtered and washed with ethanol. The residue was recrystallized from ethanol/DMSO giving compounds **1**.

2,5-Bis(4-(2,4-dichlorostyryl)phenyl)-1,3,4-oxadiazole (1a), yield 92%, m.p. 269–270 °C; ^{1}H NMR ($CDCl_3$): δ 7.11 (d, J = 16.2 Hz, 2H, CH=CH), 7.28 (d, J = 8.4 Hz, 2H, C_6H_3 5-H), 7.45 (s, 2H, C_6H_3 3-H), 7.56 (d, J = 16.2 Hz, 2H, CH=CH), 7.65 (d, J = 8.4 Hz, 2H, C_6H_3 6-H), 7.70 (d, J = 7.8 Hz, 4H, C_6H_4 3,5-H), 8.16 (d, J = 7.8 Hz, 4H, C_6H_4 2,6-H); APCI MS: m/z, 565 (M+1, 100), 567 (M+3, 54); Anal. calcd. for $C_{30}H_{18}Cl_4N_2O$ (564.3): C, 63.85; H, 3.22; N, 4.96; Found: C, 62.85; H, 3.28; N, 5.06.

2,5-Bis(4-(3,4-dichlorostyryl)phenyl)-1,3,4-oxadiazole (1b), yield 93%, m.p. 279–280 °C; ^{1}H NMR ($CDCl_3$): δ 7.13 (s, 4H, C_6H_3 5,6-H), 7.36 (d, J = 8.4 Hz, 2H, CH=CH), 7.45 (d, J = 8.4 Hz, 2H, CH=CH), 7.64 (s, 2H, C_6H_3 2-H), 7.66 (d, J = 8.4 Hz, 4H, C_6H_4 3,5-H), 8.15 (d, 4H, J = 8.4 Hz, C_6H_4 2,6-H); APCI MS: m/z, 565 (M+1, 100), 567 (M+3, 50); Anal. calcd. for $C_{30}H_{18}Cl_4N_2O$ (564.3): C, 63.85; H, 3.22; N, 4.96; Found: C, 63.29; H, 3.25; N, 5.01.

3. Results and discussion

3.1. ^{1}H NMR spectra

In the ^{1}H NMR spectra of two compounds, **1a** showed two fine doublets corresponding to the olefinic protons (CH=CH) from stilbene at δ: 7.11 ppm and 7.56 ppm (J = 16.2 Hz). At δ: 7.28, 7.65, and 7.45 ppm, two doublets and a singlet could be assigned to 5-H, 6-H and 3-H from aromatic protons (C_6H_3-protons), respectively. In addition, another two downfield doublets were also found at δ: 7.70 and 8.16 ppm which could be assigned to the contribution of aromatic protons (C_6H_4-protons). In contrast, the compound **1b** in its ^{1}H NMR spectra showed the similar resonance peaks accountable to the olefinic protons and aromatic protons (C_6H_4-protons), respectively, only a singlet was found due to 5,6-H from the benzene ring

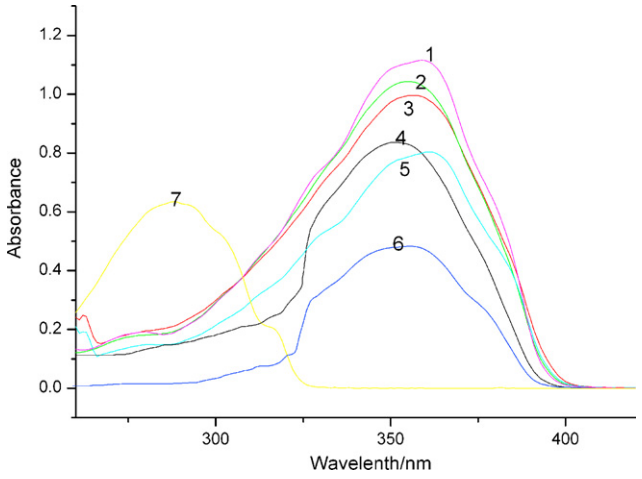

Fig. 1. UV–vis absorption spectra of the compounds **1a**, **1b** in DMF, acetone, THF compared to compound **4** in THF at room temperature (concentration: 1×10^{-5} mol/L).

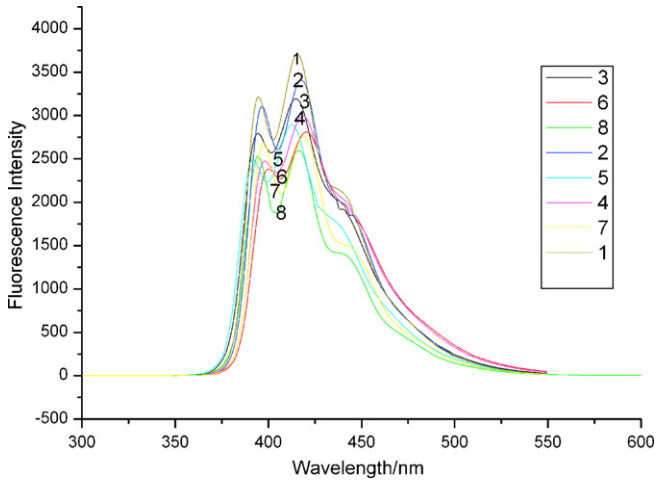

Fig. 2. Fluorescence emission spectra of the compounds **1a**, **1b** in chloroform, THF, acetone and DMF at room temperature (concentration: 1.0×10^{-5} mol/L).

(C_6H_3-protons). From the ^{1}H NMR spectra of two compounds, it was found that their olefinic protons (CH=CH) from stilbene had different coupling constant, which indicated the different substituents on benzene had an effect on proton–proton coupling.

3.2. UV–vis absorption spectra

UV–vis absorption spectra of the compounds **1a**, **1b** in DMF, acetone and THF were given in Fig. 1 at a concentration of 1.0×10^{-5} mol/L. The results are summarized in Table 1 compared to compound **4** in THF. As seen in Fig. 1 and Table 1, it was also observed that the UV–vis absorption spectra of the two compounds did not show regular variation with the polarity of solutions. The two compounds had practically the same UV–vis spectrum with only one intense and relatively narrow absorption band centred at 351–361 nm in acetone, THF and DMF, corresponding to electronic transitions of oxadiazole ring in the molecule, even if there was a shoulder in DMF for **1a** and **1b** (Fig. 1, curves 3 and 5). The maximum molar extinction coefficients of **1a** and **1b** in THF are 1.043×10^5 L mol^{-1} cm^{-1} and 1.114×10^5 L mol^{-1} cm^{-1}, respectively. By Comparison the absorption curve 7 and the other curves 1–6, it was evident that λ_{max} of compounds **1a** and **1b** in THF had a greatly shift towards higher wavelength compared to compound **4** in THF due to the increase the conjugation length of the molecule.

3.3. Fluorescence properties

Fig. 2 showed fluorescence emission spectra of two stilbene derivatives in chloroform, THF, acetone and DMF (concentration: 1×10^{-5} mol/L). The influence of solution on the fluorescence intensities of the **1a** and **1b** was investigated. We could see that the emission wavelengths of the **1a** was different in four solutions and the fluorescence intensity order in different solutions (at the same concentration) was THF (curve 2) > acetone (curve 3) > DMF (curve 6) > chloroform (curve 8). In contrast, the influence of the solution on the fluorescence intensities of **1b** was also studied. The fluorescence intensity in other solutions was also lower than that in THF (curve 1). The fluorescence intensity in chloroform was lower than those in other solutions. All these indicated that the solutions molecules had strong coordination effect and the environment played an important role in determining the fluorescence intensity of the compounds. Compared with the fluorescence characteristic emission wavelengths in four solutions, as given in Fig. 2, the two compounds had the similar emission wavelengths. In addition, the shape of emission spectra was lightly affected by the intermolecular interaction. Compared to the emission spectra of compound **4** in THF (Fig. 3), a remarkable bathochromic of the emission maximum of **1a** and **1b** was observed. The influence of concentration on fluorescence intensity of the two compounds was also studied (Fig. 4). It can be seen that the emission intensity of fluorescence were greatly decreased with gradual increasing in concentration of **1a** and **1b** in THF.

Table 2 shows the fluorescence spectra data of the two compounds **1a** and **1b** in solutions and the solid state. It is easily seen

Table 1
UV–vis absorption spectra property of **1a**, **1b**, and **4** in solution.

Compound	Solution	λ_{max} (nm)	$\times 10^{-4}$ ε_{max} (L mol^{-1} cm^{-1})
1a	DMF(3)	356	9.96
	Acetone(4)	351	8.37
	THF(2)	354	10.43
1b	DMF(5)	361	8.04
	Acetone(6)	355	4.83
	THF(1)	359	11.14
4	THF(7)	288	6.35

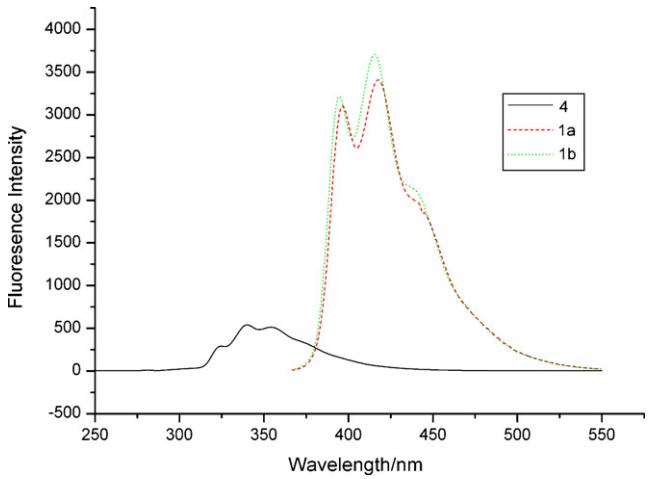

Fig. 3. Fluorescence emission spectra of the compounds **1a**, **1b** and **4** in THF (concentration: 1.0×10^{-5} mol/L).

Table 2
The fluorescence spectra data of **1a**, **1b**, and **4**.

Compound	Solution	λ_{ex} (nm)	λ_{em} (nm)	RFI[a]	Φ
	Solid state	389	452	3748	–
	DMF(6)	366	419, 400 s	2813, 2383 s	0.34
1a	Acetone(3)	360	414, 394 s	3194, 2795 s	0.42
	THF(2)	367	417, 396 s	3409, 3097 s	0.65
	$CHCl_3$(8)	362	416, 394 s	2699, 2529 s	0.50
	Solid state	430	469	2139	–
	DMF(4)	364	418, 398 s	2996, 2473 s	0.40
1b	Acetone(5)	358	412, 391 s	2893, 2493 s	0.45
	THF(1)	368	415, 394 s	3700, 3203 s	0.69
	$CHCl_3$(7)	367	418, 397 s	2762, 2681 s	0.55
4	THF	280	340, 354 s	540, 513	–

[a] RFI is relative fluorescence intensity; s: shoulder.

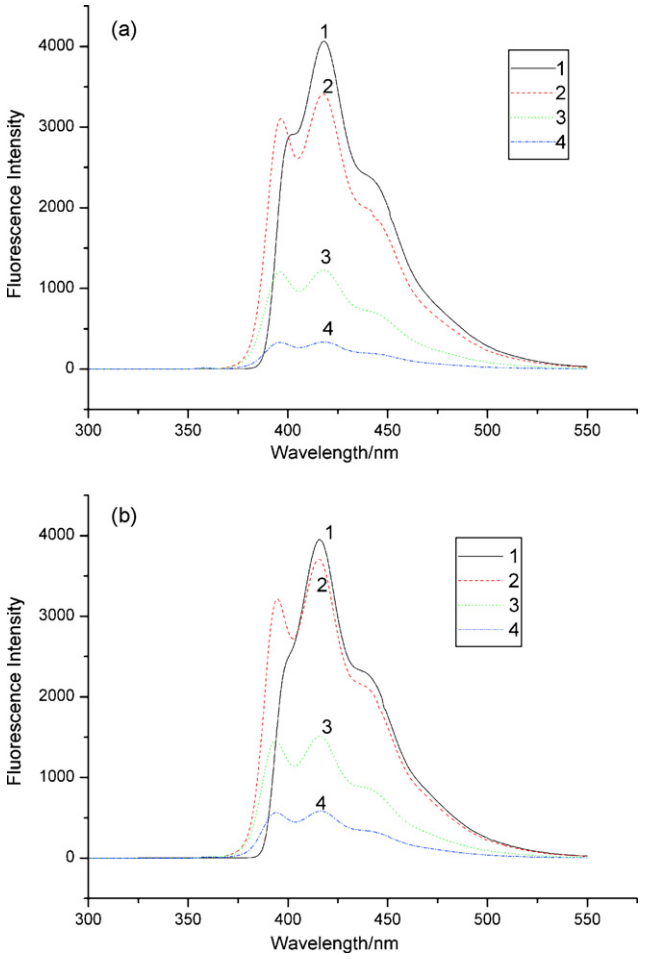

Fig. 4. Fluorescence spectra of **1a** and **1b** at different concentration of THF; 1, 1.0×10^{-4} mol/L; 2, 1.0×10^{-5} mol/L; 3, 1.0×10^{-6} mol/L; 4, 1.0×10^{-7} mol/L.

that the fluorescence quantum yield (Φ) in THF is the biggest for **1a** and **1b**, with the increase of the solution polarity, the fluorescence quantum yield (Φ) of the two stilbene derivatives decreases. This can be explained by a twisted internal charge transfer (TICT) mechanism. The decrease of the fluorescence quantum yield in polar solvents was attributed to the deactivation of the excited state by TICT, larger the solution polarity, more obvious the solution for the non-emissive "TICT" state.

4. Conclusions

Two novel stilbene derivatives were successfully synthesized, the structures of two compounds were also confirmed on the basis of MS, ^{1}H NMR, and elemental analyses. The photophysical properties had also been carried out. The results showed the two compounds exhibited strong blue fluorescence emission. The fluorescence quantum yield (Φ) of **1a** and **1b** in THF is the biggest. The influence of solution on the fluorescence intensities of the compounds indicated that the solutions and the environment played an important role in determining the fluorescence intensity of the compounds.

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References

[1] V. Cardile, L. Lombardo, C. Spatafora, C. Tringali, Bioorg. Chem. 33 (2005) 22.
[2] G. Pettit, M. Minardi, H. Rosenberg, E. Hamel, J. Nat. Prod. 68 (2005) 1450.
[3] I. Jean-Robert, M. Andrew, P.G. Mahabir, H. Kurt, J. Nat. Prod. 64 (2001) 710.
[4] M. Shapiro, R. Argauer, J. Econ. Entomol. 90 (1997) 899.
[5] R. Argauer, M. Shapiro, J. Econ. Entomol. 90 (1997) 416.
[6] C.H. Wan, J.F. Kuo, C.Y. Chen, Liq. Cryst. 27 (2000) 523.
[7] E. Wolarz, Th. Fischer, J. Stumpe, Thin Solid Films 424 (2003) 179.
[8] A.M. Machado, J.D. Da Motta Neto, R.F. Cossiello, T.D.Z. Atvars, L. Ding, F.E. Karasz, L. Akcelrud, Polymer 46 (2005) 2452.
[9] A. Momotake, T. Arai, J. Photochem. Photobiol. C: Photochem. Rev. 5 (2004) 1.
[10] J.Y. Li, D. Liu, Y.Q. Li, C.S. Lee, H.L. Kwong, S.T. Lee, Chem. Mater. 17 (2005)1208.
[11] N. Stuhr-Hansen, J.B. Christensen, N. Harrit, T. Bjornholm, J. Org. Chem. 68 (2003) 1275.
[12] Z. Fang, S. Wang, L. Zhao, Z. Xu, J. Ren, X. Wang, Q. Yang, Mater. Chem. Phys. 107 (2008) 305.
[13] Z.H. Li, P.F. Xia, K. Sun, W.C. Huang, Chin. J. Org. Chem. 2 (2002) 141.
[14] Y. Chen, C.K. Liao, T.Y. Wu, Polymer 43 (2002) 4544.
[15] C. Zhang, H. von Seggern, K. Pakbaz, B. Kraabel, H.W. Schmidt, A.J. Heeger, Synth. Met. 62 (1994) 35.
[16] Y.Q. Liu, X.Z. Jiang, Q.L. Li, D.B. Zhu, Synth. Met. 4 (1997) 36.
[17] X. Yang, Z.T. Pan, Y. Ma, J. Anal. Sci. 19 (2003) 588.