

# Synthesis and spectroelectrochemical properties of two new dithienylpyrroles bearing anthraquinone units and their polymer films

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## ARTICLE INFO

### Article history:

Received 8 June 2010

Received in revised form 5 July 2010

Accepted 5 July 2010

Available online 25 July 2010

### Keywords:

Dithienylpyrroles

Polythienylpyrroles

Aminoanthraquinone

Electropolymerization

Electrochromic materials

## ABSTRACT

Two new kinds of dithienylpyrroles bearing anthraquinone units have been prepared by the Knorr–Paal condensation between 1,4-di(thiophen-2-yl)butane-1,4-dione and 1-/2-amino-anthraquinone. The corresponding polymer films were successfully synthesized via electropolymerization. The electrochemical, electro-optical properties and electrochromic behavior of the two polymer films were further investigated by thermogravimetric analysis, cyclic voltammetry and UV–vis absorption spectra. The results demonstrated that the two polymer films were thermally stable up to nearly 300 °C. Both the two electroactive polymer films presented a stable and well-defined reversible redox process as well as multicolor electrochromic change from yellow (in the reduced state) to grey (in the neutral state) and then to blue (in the oxidized state).

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## 1. Introduction

Conducting polymers have continued to fascinate many scientists due to their synthetic accessibility and ease of modified architecture which can control the polymer's spectroelectrochemical properties. Owing to their excellent spectroelectrochemical properties, conducting polymers have been widely used in electrochromic displays [1,2] and smart windows [3], rechargeable batteries, light emitting diodes (LEDs), toxic waste cleanup, sensors, corrosion inhibitors, field effect transistors (FETs), electromagnetic interference (EMI) shielding, *etc.* [4].

Polythienylpyrrole derivatives, as a kind of hybrid conducting polymer materials, are assembled and functionalized through the central pyrrole unit to which different substituents could be introduced [5,6]. Moreover, the new hybrid polymer materials have received much attention due to their synthetic and modified accessibility, high environmental stability, long cycle life, easy processability, multichromic properties and various applications on donor–acceptor (D–A) molecular materials [7–10], electrochemical sensors [11–14], electrochromic and fluorescent materials *etc.* [15–25] in academic research.

Recently, Atilla Cihaner *et al.* [15–20] reported the synthesis of several SNS derivatives by the Knorr–Paal condensation and

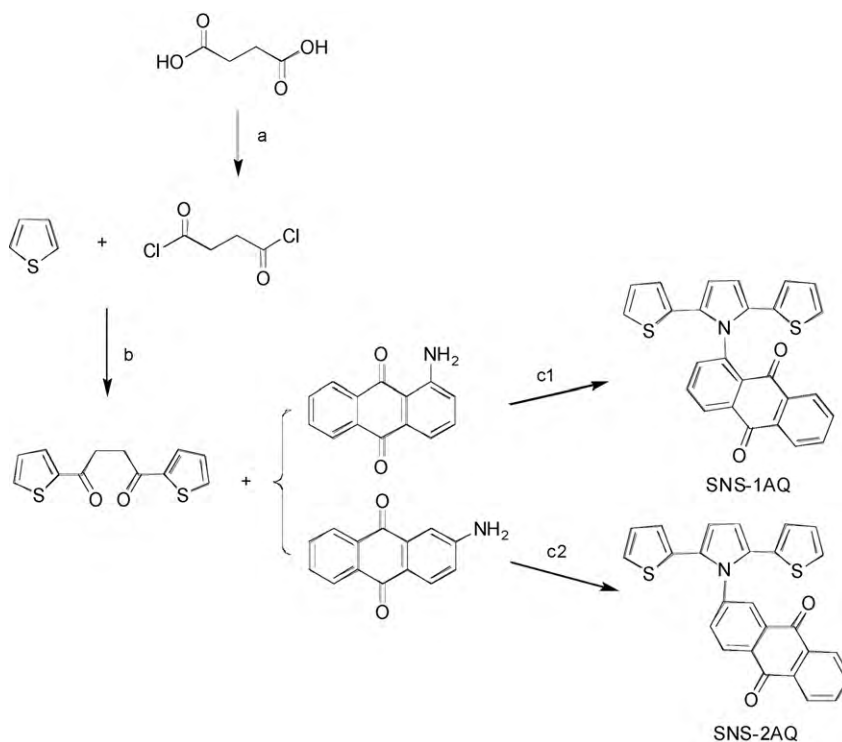
electrochemical polymerization of them which exhibited relatively lower oxidation potential (which made its electropolymerization easier and avoided over oxidation problems) and electrochromic and fluorescence properties. In addition, anthraquinone derivatives showed excellent performance on electron transfer and electrochromism *etc.* [26–30]. Based on these reports, two new hybrid materials 1-(2,5-di (thiophen-2-yl)-1H-pyrrol-1-yl)-anthraquinone (SNS-1AQ) and 2-(2,5-di (thiophen-2-yl)-1H-pyrrol-1-yl)-anthraquinone (SNS-2AQ) in which anthraquinone moieties were introduced to the central pyrrole ring of the SNS monomer, were synthesized and corresponding polymer films PSNS-1AQ and PSNS-2AQ were prepared by electropolymerization, and their spectroelectrochemical properties were also characterized and compared.

## 2. Experimental details

### 2.1. General

All chemicals and reagents used in this paper, unless otherwise specified, were purchased from Aldrich, Aladdin, and TCI Chemical Co. and used as received. All the solvents were further purified before use. All important compounds synthesized were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR and APCI-MS. <sup>1</sup>H NMR spectra were measured on a Bruker AV300 (300 MHz) spectrometer at the ambient temperature with tetramethylsilane (TMS) as an internal standard. <sup>13</sup>C NMR spectra were recorded on Bruker

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**Scheme 1.** Synthesis of 1-/2-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)-anthraquinone. (a)  $\text{SOCl}_2$ , 10 h, reflux. (b)  $\text{AlCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ , 18–20 °C, 24 h. (c1/c2) PTSA, toluene, reflux, 72 h.

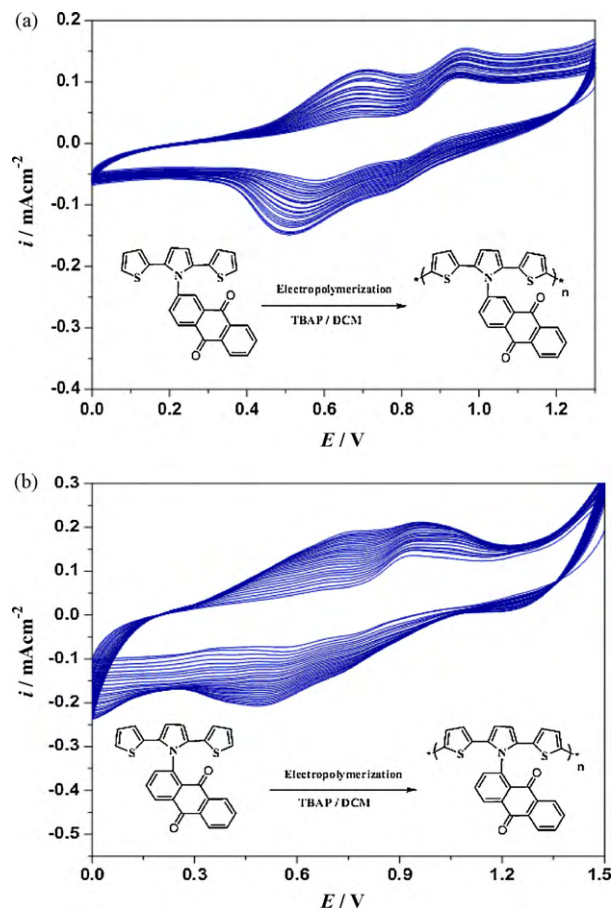
AV300 (75 MHz) spectrometer at the ambient temperature and chemical shifts were recorded in ppm from the solvent resonance employed as the internal standard. Atmospheric pressure chemical ionization mass spectra were obtained on a Bruker HCT Mass Spectrometer. Melting points were determined by differential scanning calorimetry (TAQ100) at a heating rate of 10 °C/min under Ar atmosphere. Infrared spectroscopic measurements were performed in the range 4000–400  $\text{cm}^{-1}$  on a Bruker Tensor 27 FTIR Spectrometer. UV spectra were performed on a Unicou UV-4802H UV-vis spectrophotometer connected to a computer. Thermogravimetric analysis (TGA) was performed under dynamic  $\text{N}_2$  atmosphere at a heating rate of 10 °C/min, from room temperature to 1000 °C. Cyclic voltammetry was carried out on CHI 650B electrochemical workstation using three-electrode system.

## 2.2. General procedure for the synthesis of SNS-1AQ and SNS-2AQ

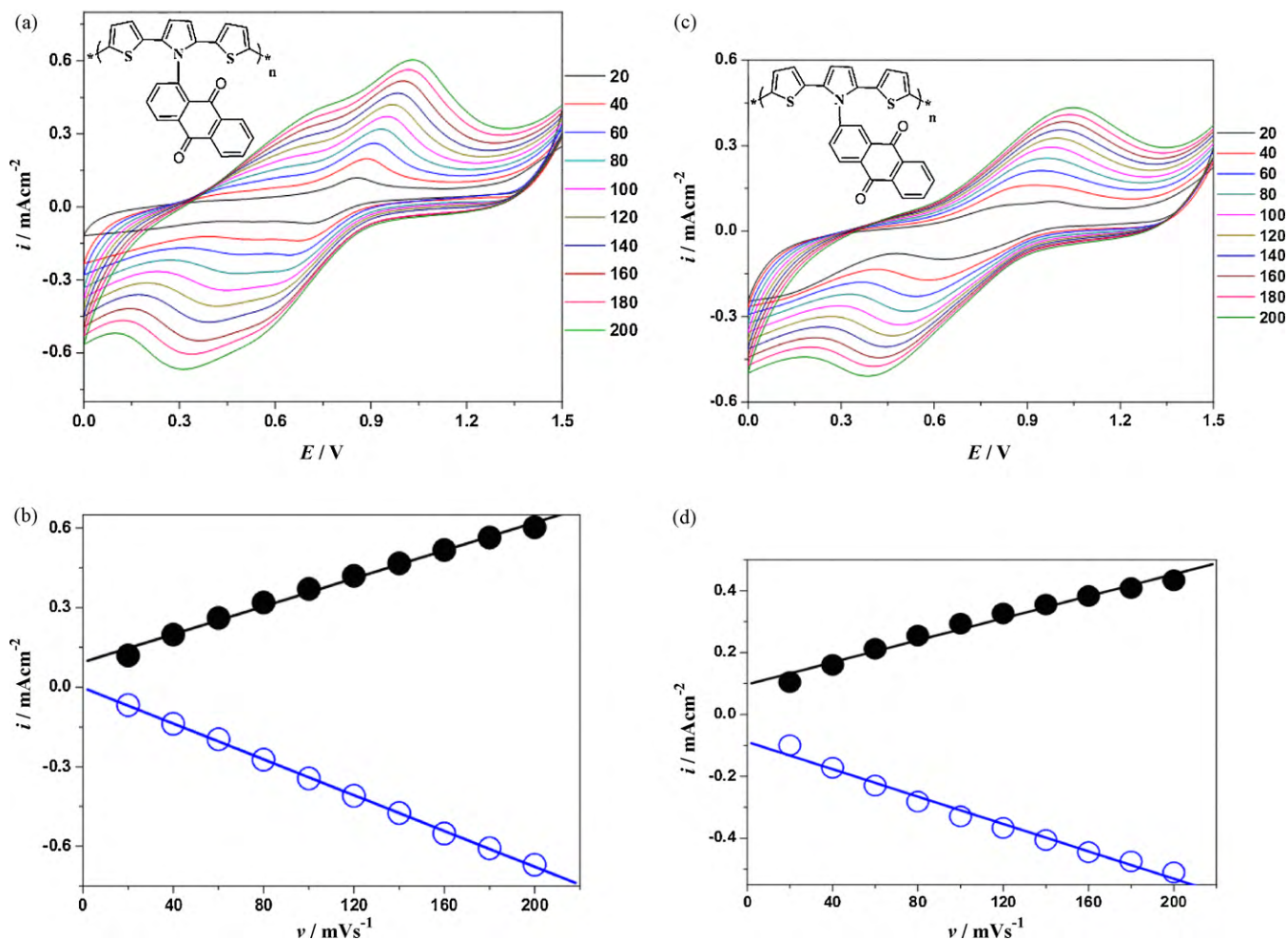
A solution of 1.0 mmol 1,4-di(thiophen-2-yl)-butane-1,4-dione [6], 1.0 mmol amine (1-aminoanthraquinone or 2-aminoanthraquinone) and 0.1 mmol p-toluenesulfonic acid in 100 mL dry toluene were heated under reflux in a Dean-Stark apparatus until all the starting materials were consumed (TLC). The flask was cooled to room temperature and the solvent was removed under reduced pressure. The resulted residue was filtered through a short pad of silica gel by eluting with DCM ( $\text{CH}_2\text{Cl}_2$ ) to give crude SNS derivatives. Then the crude product was purified by silica gel column chromatography, eluting with dichloromethane/petroleum = 2/1 (Scheme 1).

## 2.3. 1-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)-anthraquinone (SNS-1AQ)

Following the general procedure the product was obtained as an black-brown solid (yield, 48%). 223–224 °C.  $^1\text{H}$  NMR (300 M,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  8.52 (d,  $J = 7.6$  Hz, 1H), 8.23 (d,  $J = 6.3$  Hz, 1H), 8.07–8.09 (t,  $J_1 = 7.4$  Hz,  $J_2 = 5.9$  Hz, 1H), 7.81–7.86 (t,  $J_1' = 7.7$  Hz,  $J_2' = 7.7$  Hz,



**Fig. 1.** Repeated scan electropolymerization of (a) SNS-1AQ (b) SNS-2AQ in 0.01 M TBAP/DCM vs. Ag/AgCl at a scan rate of 100 mV/s.



**Fig. 2.** (a) Redox behavior of SNS-1AQ film at different scan rates and (b) relationship of anodic and cathodic current peaks as a function of scan rate in 0.01 M TBAP/DCM. (c) Redox behavior of SNS-2AQ film at different scan rates and (d) relationship of anodic and cathodic current peaks as a function of scan rate in 0.01 M TBAP/DCM.

1H), 7.70–7.74 (q, 3H), 6.95 (d,  $J=4.8$  Hz, 2H), 6.71–6.75 (t, 4H), 6.59 (d,  $J=2.7$  Hz, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta_C$  182.6, 181.1, 138.3, 137.9, 135.1, 134.5, 134.4, 134.1, 133.9, 133.8, 132.4, 131.4, 129.1, 128.9, 127.5, 126.8, 126.7, 124.7, 124.3, 110.6. FTIR (KBr, cm<sup>-1</sup>): 3107, 3085, 3070, 1670, 1580, 1411, 1315, 1279, 1162, 1111, 966, 773, 708, 687. APCI-MS ( $m/z$ ): 437(M<sup>+</sup>). UV/vis (DCM):  $\lambda_{\max 1}$  256 nm,  $\lambda_{\max 2}$  332 nm,  $\lg \epsilon_1$  4.39,  $\lg \epsilon_2$  4.15.

#### 2.4. 2-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)-anthraquinone (SNS-2AQ)

Following the general procedure the product was obtained as an orange solid (yield, 65%). 219–220 °C. <sup>1</sup>H NMR (300 M, CDCl<sub>3</sub>):  $\delta_H$  8.28–8.34 (t, 3H), 8.20 (s, 1H), 7.80–7.83 (t, 2H), 7.64 (d,  $J=8.1$  Hz, 1H), 7.08 (d,  $J=4.8$  Hz, 2H), 6.80–6.82 (t, 2H), 6.56–6.59 (t, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta_C$  182.4, 182.1, 143.8, 135.1, 134.4, 134.3, 134.1, 134.0, 133.5, 133.4, 133.0, 129.8, 128.4, 128.3, 127.4, 127.1, 125.6, 125.0, 111.2. FTIR (KBr, cm<sup>-1</sup>): 3103, 3074, 1671, 1593, 1491, 1405, 1331, 1289, 1160, 1111, 961, 766, 709, 677. APCI-MS ( $m/z$ ): 437 (M<sup>+</sup>). UV/vis (DCM):  $\lambda_{\max 1}$  255 nm,  $\lambda_{\max 2}$  327 nm,  $\lg \epsilon_1$  4.36,  $\lg \epsilon_2$  4.06.

#### 2.5. Electropolymerization and characterization

0.01 M tetrabutylammonium perchlorate (TBAP)/DCM which was distilled over CaH<sub>2</sub> under N<sub>2</sub> atmosphere) as electrolyte

solution was used to elaborate redox behavior and electropolymerization of the two monomers: SNS-1AQ and SNS-2AQ. The monomers (0.2 mM) were successfully electropolymerized via repetitive cycling voltammogram or constant potential electrolysis (1.2 V, 30 min) in three-electrode system using platinum disk (0.02 cm<sup>2</sup>) as working electrodes, platinum wire as counter electrodes and Ag/AgCl in 3 M NaCl (aq) solution as a reference.

In order to investigate the electrochemical properties exactly, the polymer films coated on the working electrodes were washed with DCM after electropolymerization to remove unreacted monomer and oligomeric species and then transferred into monomer-free electrolyte solution. The indium-tin oxide (ITO, 50  $\Omega/\square$ , 0.7 cm  $\times$  5 cm) electrodes were used as substrate for the polymer films to deposition. UV–vis spectra and cyclic voltammetry were used to investigate spectroelectrochemical measurements which were carried out to consider absorption spectra of the polymer films under applied voltage. The spectroelectrochemical cell was made up of three-electrode system including a quartz cuvette, an Ag wire (pseudo-RE) which was calibrated externally using a 1 mM solution of ferrocene/ferrocenium coupled in an electrolyte solution, Pt wire counter electrode (CE) and ITO glass as transparent working electrode (WE). The polymer films on the ITO glass were switched between neutral and doped states several times in monomer-free electrolyte solution (TBAP/DCM) to study the electrochemical redox behavior, electro-optical properties and reversibility.



### 3. Results and discussion

#### 3.1. Electropolymerization of SNS-1AQ and SNS-2AQ

In order to study the redox behaviors of the two polymer films, the corresponding monomers were scanned electropolymerization via cyclic voltammetry. As the electropolymerization time increased, the thickness of PSNS-1AQ and PSNS-2AQ film increased and their colors changed from light brown-grey to light violet then to blue-violet. It was reported that the oxidation of dithienylpyrrole systems do not significantly affected by the groups substituted on the N-position of the central pyrrole ring [15,16,18]. As shown in Fig. 1, in the first cycle, a single irreversible oxidation peak was observed for SNS-1AQ and SNS-2AQ at 0.95 V and 0.94 V, respectively. The results were well in agreement with the redox behavior of SNS ( $E_{ox} = 0.94$  V) reported by Ferraris and Hanlon [29]. This result confirmed that anthraquinone units had no contributions to the electronic structure of the dithienylpyrrole trimeric system. Moreover, a new reversible redox couple was observed after repeated cycle and the current value of this reversible peak continued to intensify after consecutive cycles for the two monomers, which was attributed to the formation of an electroactive polymer.

As seen in Fig. 2, the polymer films exhibited a single and well-defined reversible redox couple ( $E_{p,1/2}$ ) that was centered at about 0.7 V for PSNS-1AQ and 0.58 V for PSNS-2AQ. In addition, both of the two polymer films retained their promising reversible and well-defined properties even at higher scan rates or after hundreds of cycles between their redox states (reduced and oxidized states). Furthermore, it was found that both anodic and cathodic current responses of the two polymer films increased linearly as the scan rate increased, which demonstrated that the redox process was non-diffusional and the electroactive polymers were well adhered to the working electrodes surface [15–18,23–25].

#### 3.2. FTIR study

It was reported that there were three characteristic peaks of SNS units at  $679\text{ cm}^{-1}$  for  $\alpha$ -H of thiophene rings,  $770\text{ cm}^{-1}$  for  $\beta$ -H of pyrrole ring and  $843\text{ cm}^{-1}$  for  $\beta/\beta'$ -H of thiophene rings in SNS derivatives and the analogous peaks were observed at  $687\text{ cm}^{-1}$ ,  $772\text{ cm}^{-1}$ ,  $845\text{ cm}^{-1}$  and  $676\text{ cm}^{-1}$ ,  $766\text{ cm}^{-1}$ ,  $843\text{ cm}^{-1}$  in SNS-1AQ and SNS-2AQ, respectively [15–20]. Comparing with the monomers, the FTIR spectra of the polymers revealed that electropolymerization mainly proceeded via SNS units and anthraquinone subunits remained unchanged during polymerization. For example, in the spectra of the PSNS-1AQ and PSNS-2AQ, the disappearance of the peaks at  $687\text{ cm}^{-1}$ ,  $676\text{ cm}^{-1}$  and  $3106\text{ cm}^{-1}$ ,  $3103\text{ cm}^{-1}$  which were attributed to  $\alpha$ -H of thiophene rings in the monomers of SNS-1AQ and SNS-2AQ, confirmed the  $\alpha$ -coupling between the external thiophene rings. Therefore, the corresponding polymers had linear chains due to the proceeding polymerization via  $\alpha$ - $\alpha$  linkages. However, all the other peaks in the spectra of the polymer films almost remained unchanged upon polymerization, but with some peaks weakened, widened and red shifted, which unambiguously indicated the presence of anthraquinone subunits in the polymer backbone:  $3070\text{ cm}^{-1}$  (Ar,  $=\text{C-H}$ )<sub>s</sub>,  $1670\text{ cm}^{-1}$  (C=O)<sub>s</sub>,  $1580\text{ cm}^{-1}$  and  $1470\text{ cm}^{-1}$  (Ar, C=C)<sub>s</sub>,  $1112\text{ cm}^{-1}$  (C-O)<sub>s</sub>,  $807\text{ cm}^{-1}$  (Ar,  $=\text{C-H}$ )<sub>8</sub> (1,2,3-substituted benzene ring),  $772\text{ cm}^{-1}$  (Ar,  $=\text{C-H}$ )<sub>8</sub> (1,2-substituted benzene ring) for PSNS-1AQ, while  $3074\text{ cm}^{-1}$  (Ar,  $=\text{C-H}$ )<sub>s</sub>,  $1671\text{ cm}^{-1}$  (C=O)<sub>s</sub>,  $1593\text{ cm}^{-1}$  and  $1490\text{ cm}^{-1}$  (Ar, C=C)<sub>s</sub>,  $1110\text{ cm}^{-1}$  (C-O)<sub>s</sub>,  $884\text{ cm}^{-1}$  and  $801\text{ cm}^{-1}$  (Ar,  $=\text{C-H}$ )<sub>8</sub> (1,2,4-substituted benzene ring),  $766\text{ cm}^{-1}$  (Ar,  $=\text{C-H}$ )<sub>8</sub> (1,2-substituted benzene ring) for PSNS-2AQ. In addition, the strong peaks at  $1089\text{ cm}^{-1}$ ,  $625\text{ cm}^{-1}$  and  $1092\text{ cm}^{-1}$ ,  $622\text{ cm}^{-1}$  in the two polymer spectra were due to the presence of  $\text{ClO}_4^-$  dopant [15,16,18,19,23] (Fig. 3).

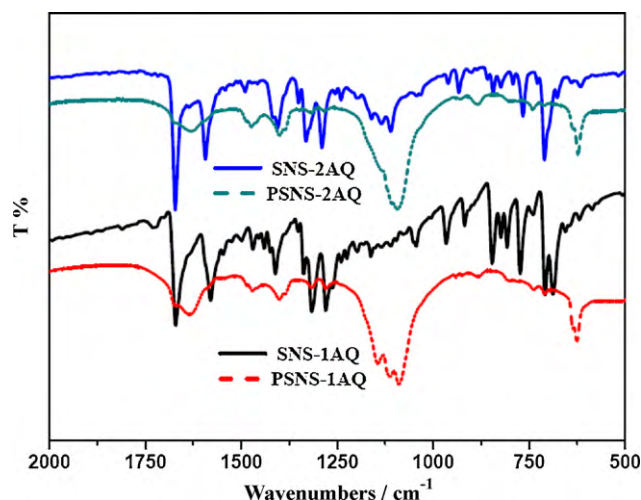


Fig. 3. FTIR spectra of SNS-1AQ and SNS-2AQ as well as their corresponding polymers.

#### 3.3. Thermogravimetric analysis of PSNS-1AQ and PSNS-2AQ

Fig. 4 showed the high-resolution TGA curves of the two polymers at a heating rate of  $10^\circ\text{C}/\text{min}$ , from room temperature to  $1000^\circ\text{C}$ . The three curves reflected the whole weight-loss process of the two polymers. An initial weight loss was observed in the TG curve for the two polymers between room temperature and about  $150\text{--}200^\circ\text{C}$  that could be assigned to the loss of variable amounts of solvent or water adsorbed or loosely bonded to the polymer chains. The percentage assigned to the solvent/water loss was about 1% for PSNS-1AQ and 0.7% for PSNS-2AQ, respectively. The polymers were stable up to nearly  $300^\circ\text{C}$  where the first significant weight loss

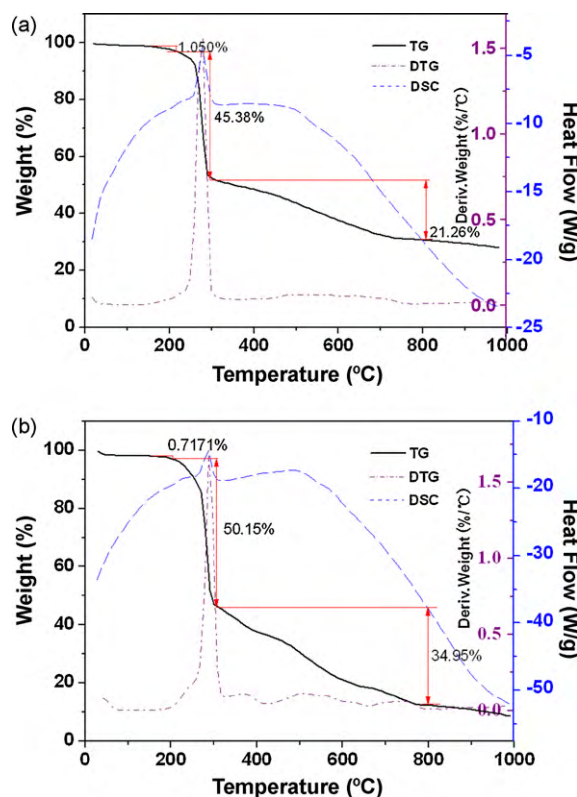
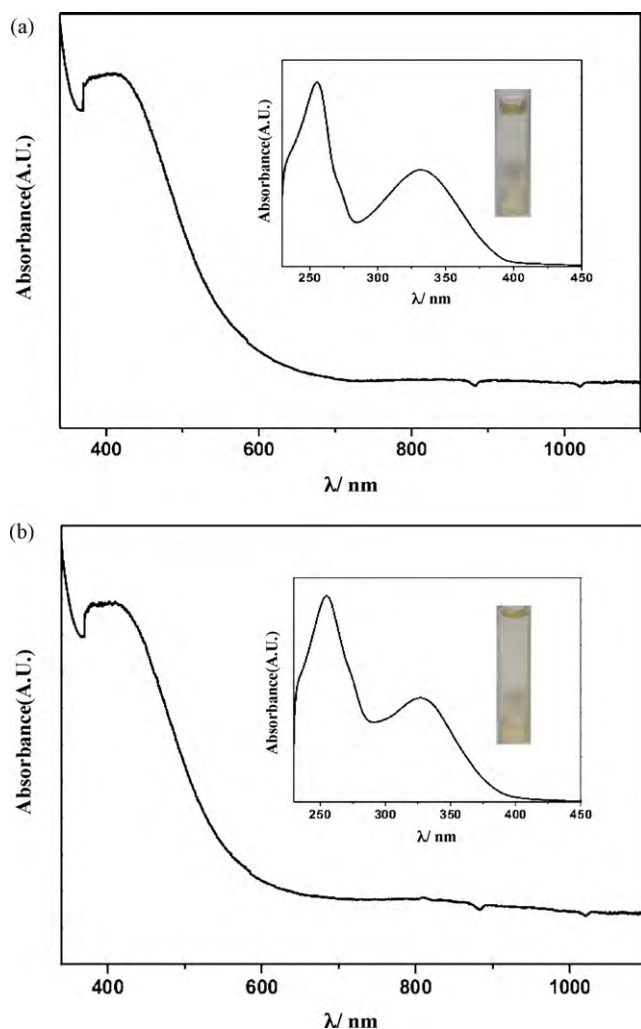


Fig. 4. High-resolution TGA of (a) PSNS-1AQ and (b) PSNS-2AQ under nitrogen atmosphere. Heating rate:  $10^\circ\text{C}/\text{min}$  from room temperature to  $1000^\circ\text{C}$ .

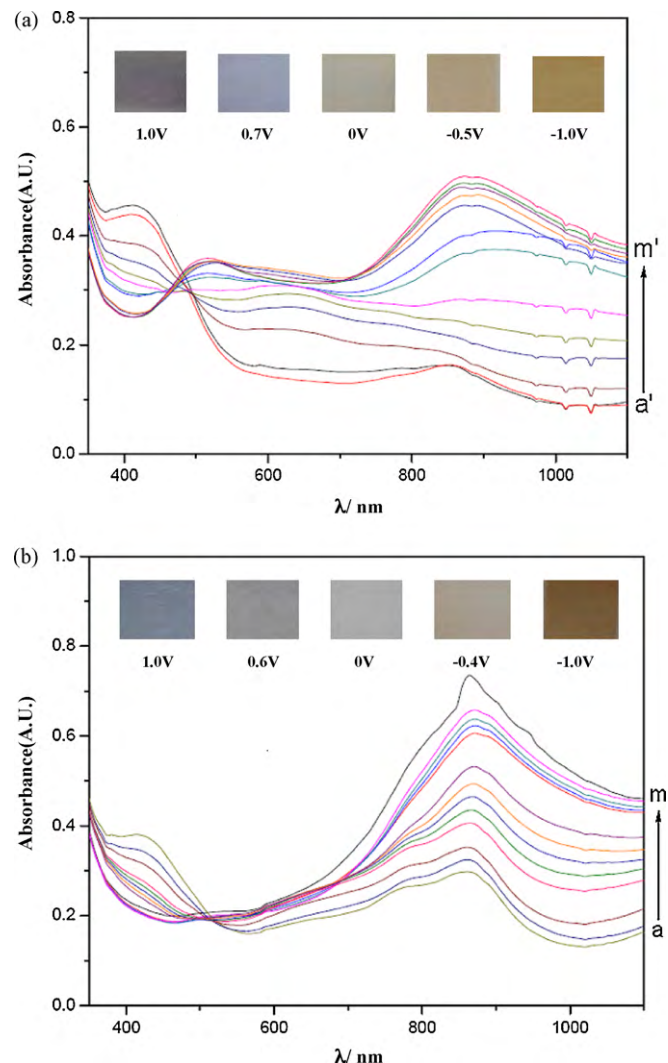


**Fig. 5.** UV-vis absorption spectra of (a) PSNS-1AQ and (b) PSNS-2AQ films on ITO glass. Inset: UV-vis absorption spectra and photos of (a) PSNS-1AQ and (b) PSNS-2AQ in DCM.

(in the TG and DTG curves) corresponding to a strong calorimetric absorption peak (in the DSC curve) was observed. This weight loss (about 45% and 50% for PSNS-1AQ and PSNS-2AQ in the range of 200–300 °C) could be tentatively attributed to the lack of dopant as it was explained in similar research work based on conducting polymers [31]. After the dopant loss step, the two polymers showed a constant decrease of weight (about 21% and 34% for PSNS-1AQ and PSNS-2AQ in the range of 300–800 °C) due to the degradation of the polymer backbone. The residue of the different polymers at 800 °C was 12% for PSNS-1AQ and 31% for PSNS-2AQ. The two polymers were found to be very stable against to thermal effect. Comparing to PSNS-1AQ, PSNS-2AQ film was more stable against to thermal effect possibly due to stereo-hindrance effect which decreased the stability of the molecule structure of PSNS-1AQ.

#### 3.4. Spectroelectrochemistry properties of PSNS-1AQ and PSNS-2AQ

The absorption spectra of PSNS-1AQ and PSNS-2AQ films on ITO glass (in the neutral state), together with that of the corresponding monomers in DCM, were represented in Fig. 5, inset. The absorption maximum ( $\lambda_{\max}$ ) in the spectra of monomers PSNS-1AQ and PSNS-2AQ were similar (256, 332 nm and 255, 327 nm in DCM which were due to the  $\pi$ - $\pi^*$  transition of the anthraquinone and SNS moieties, respectively). Also, for the corresponding electrochem-



**Fig. 6.** (a) UV/vis/NIR spectroelectrochemistry for PSNS-1AQ on ITO glass; Pt wire counter electrode, Ag/AgCl reference electrode, TBAP/DCM supporting electrolyte (0.01 M): (a') -1.2 V; (b') -1.0 V; (c') -0.8 V; (d') -0.6 V; (e') -0.4 V; (f') -0.2 V; (g') 0 V; (h') 0.2 V; (i') 0.4 V; (j') 0.6 V; (k') 0.8 V; (l') 1.0 V; (m') 1.2 V. Inset: Multichromatic behavior of PSNS-1AQ at +1.0 V (dark blue-purple), +0.7 V (light blue-purple), 0 V (light yellow-green), -0.5 V (light yellow), -1.0 V (orange-yellowish). (b) UV/vis/NIR spectroelectrochemistry for PSNS-2AQ on ITO glass; Pt wire counter electrode, Ag/AgCl reference electrode, TBAP/DCM supporting electrolyte (0.01 M): (a) -1.2 V; (b) -1.0 V; (c) -0.8 V; (d) -0.6 V; (e) -0.4 V; (f) -0.2 V; (g) 0 V; (h) 0.2 V; (i) 0.4 V; (j) 0.6 V; (k) 0.8 V; (l) 1.0 V; (m) 1.2 V. Inset: Multichromatic behavior of PSNS-2AQ at +1.0 V (blue-grayish), +0.6 V (light blue-grayish), 0 V (light gray), -0.4 V (light yellow-grayish), -1.0 V (dark orange-yellowish). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

ically deposited polymer films, PSNS-1AQ and PSNS-2AQ exhibited similar  $\lambda_{\max}$  (corresponding to the  $\pi$ - $\pi^*$  transition) at 411 nm and 414 nm respectively. As seen in Fig. 5, the absorption bands belonging to SNS moiety shifted from 332 nm and 327 nm in the two monomers to 411 nm and 414 nm in the corresponding polymers. However, the absorption band of anthraquinone moiety was not affected by the polymerization. The  $\lambda_{\max}$  of the polymer was much higher than that of the corresponding monomer, which was caused by increasing of the conjugation length in the polymer. And this is a typical trend in conducting polymers [31].

The optical band gap of polymeric products was calculated from their low energy absorption edges ( $\lambda_{\text{onset}}$ ) according to Planck equation ( $E_g = 1241/\lambda_{\text{onset}}$ ) [32]. It was observed that the  $\lambda_{\max}$  and  $\lambda_{\text{onset}}$  of the absorption spectra of PSNS-1AQ were at 411 nm and

**Table 1**

Electrical and optical data for SNS derivatives and their polymers.

Polymer	$E_{m,ox}$ (V)	$E_{p,1/2}$ (V)	$\lambda_p$ (nm)	$E_g$ (eV)	Reduced state	Oxidized state
PSNS	0.94	0.6	430	2.61	Yellow orange	Dark blue
PSNS-1AQ	0.95	0.7	414	2.20	Dark orange-yellowish	Dark blue-purple
PSNS-2AQ	0.94	0.58	411	2.13	Dark yellow	Dark blue-purple

588 nm, corresponded to a band gap of 2.11 eV. While for PSNS-2AQ, the  $\lambda_{max}$  and  $\lambda_{onset}$  of the absorption spectra were observed at 414 nm and 596 nm, corresponded to a band gap of 2.08 eV. As shown in Table 1, the  $E_g$  values are 2.11 and 2.08 eV for PSNS-1AQ and PSNS-2AQ, respectively, which were smaller than that of the unsubstituted PSNS ( $E_g = 2.61$  eV) [17].

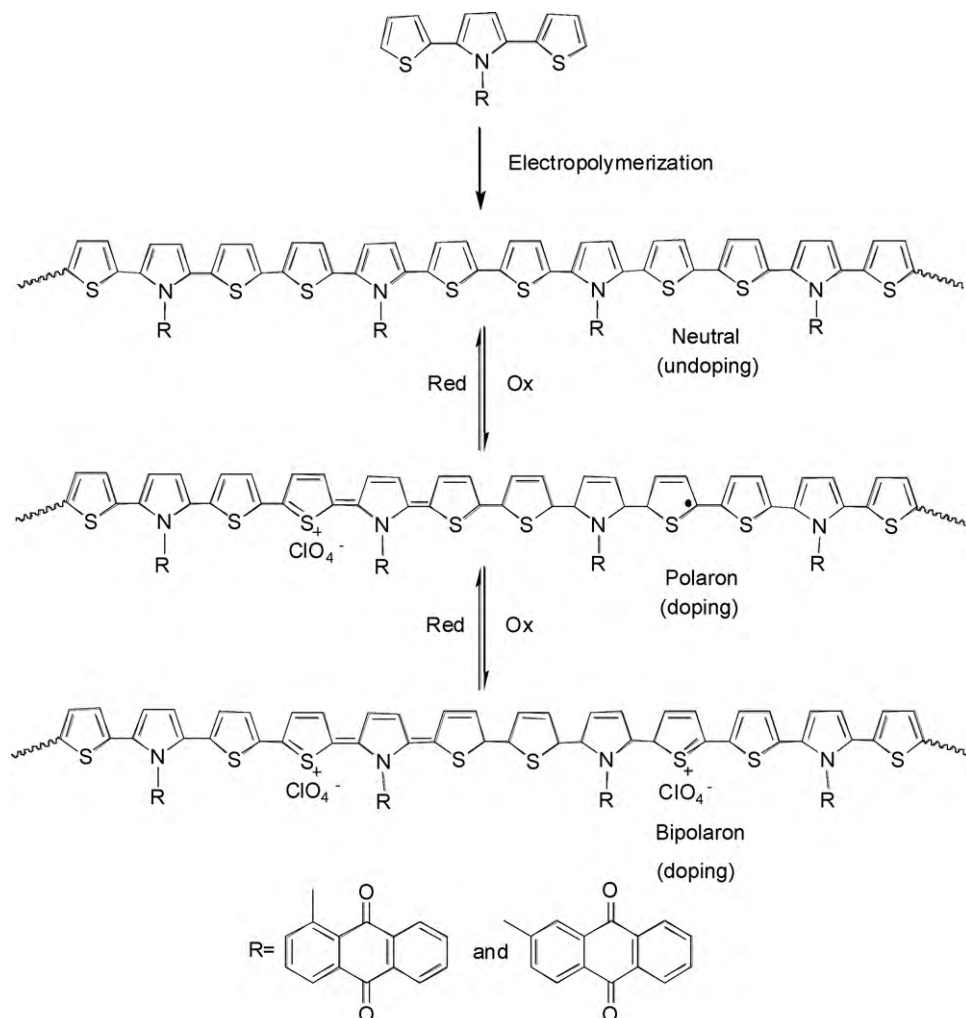
Spectroelectrochemical study on PSNS-1AQ and PSNS-2AQ film was carried out by varying the voltage between +1.2 V and −1.2 V. For monitoring the electrochromic process, five potential points were chosen for each of the two polymer films and corresponding electrochromic photos were taken and recorded. Both of the two polymers revealed multicolor electrochromism exhibiting several colored states between yellow (in the reduced state), grey (in the neutral state) and blue (in the oxidized state) (Fig. 6a and b). Moreover, it was found that when the voltage applied to PSNS-1AQ film, the valance band-conduction band ( $\pi-\pi^*$  transition) at 411 nm was diminished and another three bands intensified at 520 nm, 650 nm and 900 nm. While to PSNS-2AQ film, the valance band-conduction band ( $\pi-\pi^*$  transition) diminished at 414 nm and

another two bands intensified at 780 nm and 890 nm. For the two polymer films, the five intensified bands indicated the formation of polarons and bipolarons on the polymer backbone (Scheme 2), respectively [16–18,22,25].

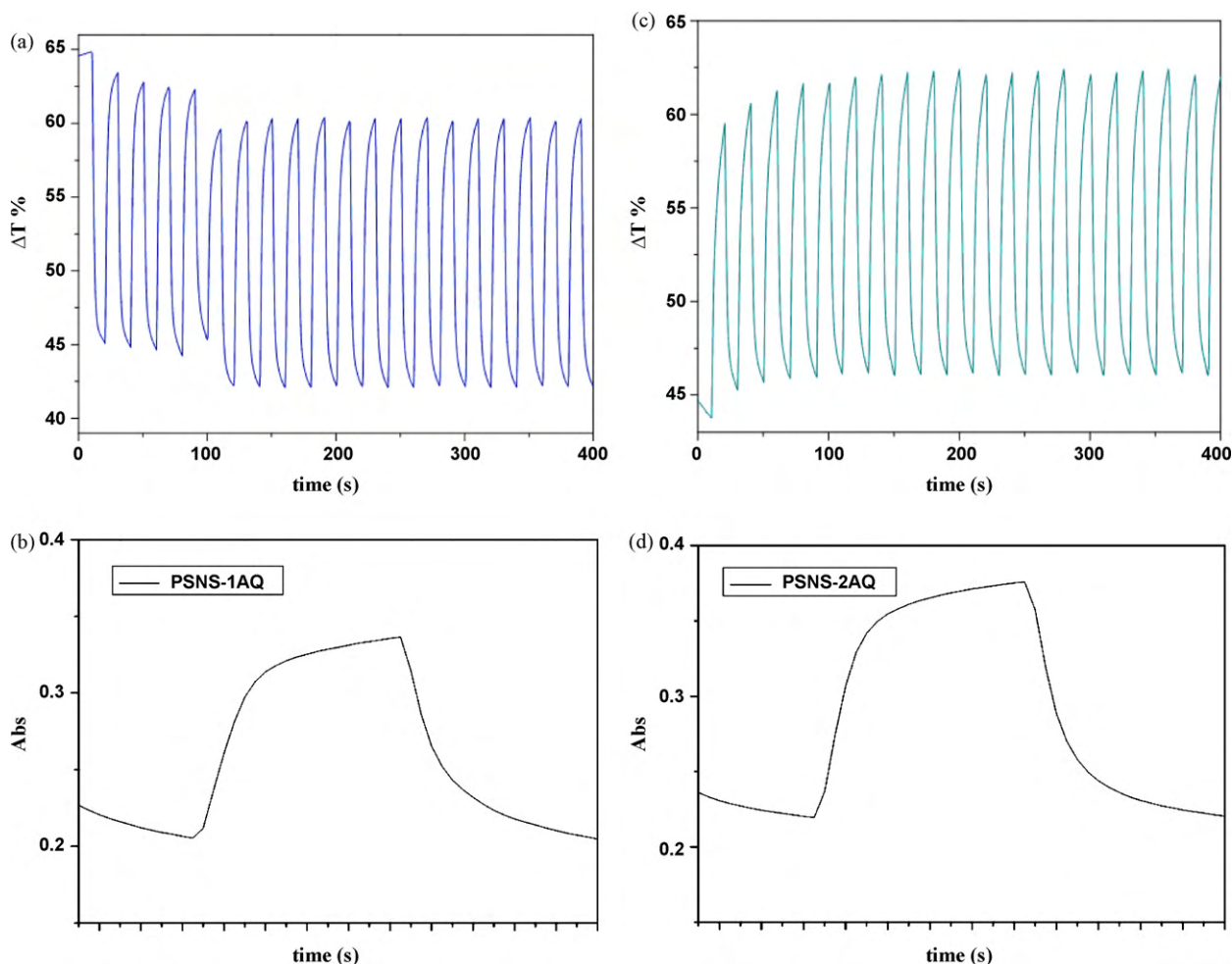
### 3.5. Switching and stability of PSNS-1AQ and PSNS-2AQ

Switching and stability are two important properties of an electrochromic material. In order to investigate these properties, the PSNS-1AQ and PSNS-2AQ film were switched by repeated potential steps between the reduction (−1.0 V) and oxidized states (+1.0 V) with a residence time of 10 s in the electrolyte solution.

The optical contrast is given as the transmittance difference between the reduced and oxidized states and is reported as  $\Delta T\%$  which was monitored as a function of time at the wavelength in the visible region. The maximum  $\Delta T\%$  in the visible region (at 780 nm) was found 18% for PSNS-1AQ and 16.5% for PSNS-2AQ, respectively. As seen in Fig. 7, the transmittance–time curves for the two polymer films started to be stable after several repeated potential

**Scheme 2.** The electropolymerization doping and redox process of SNS-1AQ and SNS-2AQ.





**Fig. 7.** (a) Optical transmittance changes and (b) optical switching studies for PSNS-1AQ film was monitored at 780 nm in 0.1 M TBAP/DCM. (c) Optical transmittance changes and (d) optical switching studies for PSNS-2AQ film was monitored at 780 nm in 0.1 M TBAP/DCM.

steps. This result was possibly due to the doping–undoping process (Scheme 2) which needed some time to become stable. Quantification of switching time was performed by defining a change in 95% of the total absorbance span, since the naked eye could not distinguish the color change after this point. The optical response time in PSNS-1AQ was approximately 4 s for the oxidation process (blue-grayish) and approximately 4 s for the reduction process (dark orange-yellowish) while PSNS-2AQ needed also approximately 3 s to be oxidized (dark blue–purple) and approximately 3 s to be reduced (orange-yellowish).

It was found that both of the two polymer films showed a parallel coloring and bleaching process, which meant a parallel kinetics of dopant diffusion in the oxidation and reduction process. However, both polymers presented fast switching time in the range of a few seconds, and the slight discrepancy in the time required to achieve 95% of the coloring and decoloring states may be due to the conditions of electrodeposition and the resulting thickness of the polymer films [31].

Furthermore, the optical density ( $\Delta OD$ ) and colouration efficiency (CE) at 780 nm can be calculated using the following equations [33].

$$\Delta OD = \log \frac{T_{\text{colored}}}{T_{\text{bleached}}} \quad \text{and} \quad CE = \frac{\Delta OD}{Q_d}$$

where  $Q_d$  is the injected/ejected charge during a redox step;  $T_{\text{colored}}$  and  $T_{\text{bleached}}$  are the transmittance in the oxidized and neutral states, respectively. On the basis of these equations, the  $\Delta OD$  and

CE was calculated to be 0.15 and 105 cm<sup>2</sup>/C for PSNS-1AQ, 0.13 and 98 cm<sup>2</sup>/C for PSNS-2AQ, respectively.

#### 4. Conclusions

In summary, two new dithienylpyrrole compounds bearing anthraquinone units (SNS-1AQ and SNS-2AQ) were synthesized by the Knorr–Paal condensation, corresponding polymer films PSNS-1AQ and PSNS-2AQ were prepared by electropolymerized. All the dithienylpyrrole hybrid compounds and polymer films were well characterized. The polymer films PSNS-1AQ and PSNS-2AQ were studied comparatively and which were found that PSNS-1AQ and PSNS-2AQ films performed similar spectroelectrochemical properties. Both of the two polymer films were thermally stable up to nearly 300 °C, and showed a well-defined reversible redox process and stable electrochromic behavior (yellow in the reduced state, grey in the neutral state and blue in the oxidized state) which can make them amenable for electrochromic devices.

#### Acknowledgements

All authors herein are grateful to the support from National Ministry of Science and Technology Innovation Fund for High-tech Small and Medium Enterprise Technology (No. 09C26215112399) and National Ministry of Human Resources and Social Security Start-up Support Projects for Students Returned to Business, Office of Human Resources and Social Security Issued 2009 (143).

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