Journal of Solid State Electrochemistry (2020) 24:441–445
https://doi.org/10.1007/s10008-019-04343-0

ORIGINAL PAPER

Blue-to-transmissive electrochromic poly(2,3-dimethyl-2,3-dihydrothieno[3,4-b][1,4]dioxine) (PEDOT-Me_2) with improved optical contrast

Xiaoming Chen [1] · **Jingyan Zhang** [1]

Received: 25 January 2019 / Revised: 1 July 2019 / Accepted: 8 July 2019 / Published online: 18 July 2019

Abstract

A novel electrochromic polymer poly(2,3-dimethyl-2,3-dihydrothieno[3,4-b][1,4]dioxine) (PEDOT-Me_2) based on 3,4-ethylenedioxythiophene (EDOT) with symmetric dimethyl pendant groups was successfully synthesized through electrochemical polymerization in 0.1 M $LiClO_4$/ACN electrolyte. The polymer film displays reversible electrochromism switching between blue neutral state (− 1.2 V) and transmissive sky blue oxidized state (0.5 V) with an enhanced optical contrast ($\Delta T = 30\%$) in comparison with the traditional PEDOT ($\Delta T = 25\%$).

Keywords Blue · Transmissive · Electrochromic polymer

Introduction

Electrochromism is a reversible change in optical properties that can occur when a material is electrochemically oxidized (loss of electrons) or reduced (gain of electrons). Conjugated polymers are one of the most popular electrochromic materials because of their good optical contrast, fast switching speed, and high coloration efficiency, which make them suitable to be utilized in various real-world applications such as smart windows and display panels [1–3]. As effective electrochromes, the most attractive merit of conjugated polymers is that the electrochromic properties can be tuned through chemical modification of conjugated backbones [4] or side chains [5].

Colored-to-transmissive electrochromic polymers are long-lived aspirations in electrochromic applications because, in most cases, a material which has a transmissive redox state is required for window or display applications where multiple chromophores can be incorporated and overlaid to get new colors [6]. As a blue-to-transmissive electrochromic polymer, poly(3,4-ethylenedioxythiophene) (PEDOT) and its derivatives consist a series of the most famous products in organic electronics [7]. Traditional PEDOT has a very high conductivity, is almost transparent in its oxidized state, and has a very high stability. However, to the best of our knowledge, it is a pity that the transmittance change (ΔT) between its neutral state and oxidized state is very low (25%) [8].

To fine tune the electrochromic properties of conjugated polymer, designing and preparing new corresponding monomers is an effective approach. Reynolds group found that the optical contrast, i.e., the transmittance change (ΔT) of PEDOT, can be improved by increasing the alkylenedioxythiophene ring size or by incorporating substituents [9]. As in the former case, the most successfully developed PEDOT derivative is poly(3,3-dimethyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine) (PProDOT-Me_2) which is symmetrically substituted by two methyl groups on the central carbon of the propylene bridge. It shows an outstanding optical contrast of 78% at 578 nm [9]. While in the latter case, the reports in literatures on PEDOT derivatives by incorporating pendant groups on ethylenedioxy bridge are relatively not so much.

In this paper, the electrochemical synthesis of a homopolymer poly(2,3-dimethyl-2,3-dihydrothieno[3,4-b][1,4]dioxine) (PEDOT-Me_2) based on PEDOT derivative with symmetrically di-substituted methyl groups on the carbon atoms of the ethylenedioxy bridge was reported. We hope that introducing symmetric methyl groups to the polymer chain will increase the interchain spacing and therefore improve the optical contrast,

Dedicated to the memory of Ivo Alexandre Hümmelgen

✉ Xiaoming Chen
chenxmyn@hotmail.com

[1] Anhui Key Laboratory of Advanced Building Materials, School of Materials & Chemical Engineering, Anhui Jianzhu University, Hefei 230601, People's Republic of China

i.e., the transmittance change (ΔT) of PEDOT. The results indicate that PEDOT-Me_2 film has a reversible electrochromism switching between blue and transmissive sky blue under externally applied potentials (− 1.2 V and 0.5 V) with an enhanced ΔT = 30%.

Experimental

Materials

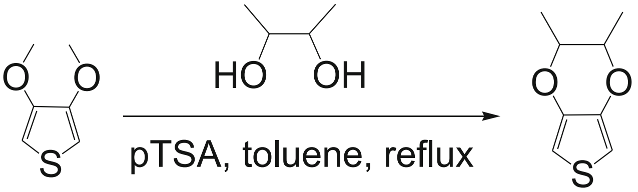
3,4-Di(methoxy)thiophene (DMOT), 2,3-butanediol, and lithium perchlorate ($LiClO_4$, 99%) were from Aladdin Industrial Inc. Acetonitrile (ACN, HPLC), propylene carbonate (PC, AR), and all other chemicals were bought from Sinopharm Chemical Reagent. All reagents were used as received.

Instruments

NMR spectra were collected on a 400-MHz Bruker Avance 400 spectrometer in deuteriochloroform ($CDCl_3$). IR spectra were determined using NICOLET 6700 FTIR spectrometer (Thermo Scientific). Cyclic voltammetry, spectroelectrochemistry, and colorimetry studies were performed using a CHI600E electrochemical analyzer and Persee General T6 UV-Vis-NIR spectrometer.

Synthesis of 2,3-dimethyl-2,3-dihydrothieno[3,4-b][1,4]dioxine (EDOT-Me_2)

The synthetic route of EDOT-Me_2 is shown in Scheme 1. In a 250-mL round bottom flask with a Soxhlet extractor with type 4 Å molecular sieves, the reaction mixture consisting of DMOT (14 mmol, 2.02 g), 2,3-butanediol (20 mmol, 1.8 g), p-toluenesulfonic acid monohydrate (pTSA, 1.4 mmol, 0.266 g), and 150 mL toluene was loaded. The reaction mixture was refluxed for 24 h and then washed with deionized water for three times. By rotary evaporation under vacuum, the solvent was removed. The residue was subjected to column chromatography (petroleum ether/ethyl acetate = 30:1, *v*/*v*) to give the final product as a yellow oil 0.6 g (25% yield). ^1H NMR (400 MHz, $CDCl_3$, δ): 6.30 (q, 2H), 4.27 (m, 2H), 1.31 (d, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 142.2, 141.5, 99.3, 99.3, 70.0, 69.5, 16.3.



Scheme 1 The synthesis of EDOT-Me_2

Electrochemical synthesis of the polymer PEDOT-Me_2

The synthetic route is depicted in Scheme 2. Electropolymerization of EDOT-Me_2 was carried out following the procedures reported by us previously [10, 11].

Electrochemical and spectroelectrochemical characterization

The electrochemical and spectroelectrochemical characterizations were carried out in an electrochemical cell consisting of an ITO/glass (4 cm × 0.7 cm, sheet resistance < 7 Ω/sq), a Pt wire, and an Ag wire, as has been done in our previous studies [12, 13]. Monomer-free $LiClO_4$/PC solution was utilized as the supporting electrolyte.

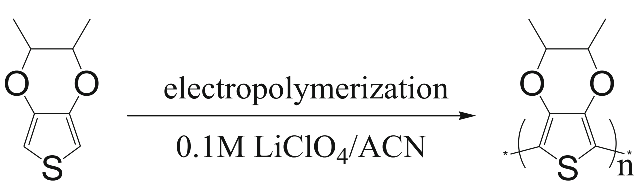
Results and discussion

Electrochemical polymerization

EDOT-Me_2 (0.01 M) in 0.1 M $LiClO_4$/ACN solution was subjected to repeated cyclic voltammetry (CV) scans between 0 and 1.8 V at a potential scan rate of 100 mV/s for 5 cycles as presented in Fig. 1. It can be seen in Fig. 1 that, in the first CV cycle when the potential is beyond 1.3 V, the current exhibits a sharp increase, indicating the oxidation of the monomer EDOT-Me_2 occurs. Upon repeated CV scans, a new redox wave between 0 and 0.5 V can be found which is due to the redox of the polymer PEDOT-Me_2. The current of each CV cycle increases with the cycle number, indicating that there was a film of redox-active and conductive polymer on the ITO-coated glass slide and the amount of the electrodeposited polymer increased with the cycle number of CV.

Polymer characterization

The FTIR spectra of EDOT-Me_2 and the corresponding polymer PEDOT-Me_2 are shown in Fig. 2a and b respectively. It can be seen in Fig. 2a the characteristic absorption peaks of the monomer EDOT-Me_2 displayed. The sharp but relatively weak absorption peak at 3110 cm^{-1} is corresponding to CH group in the thiophene ring; the strong absorption peaks at 2980 cm^{-1} (ν_{as}) and 2937 cm^{-1} (ν_s) are corresponding to CH_3 groups in the side chain; the relatively strong peak at



Scheme 2 The synthesis of PEDOT-Me_2

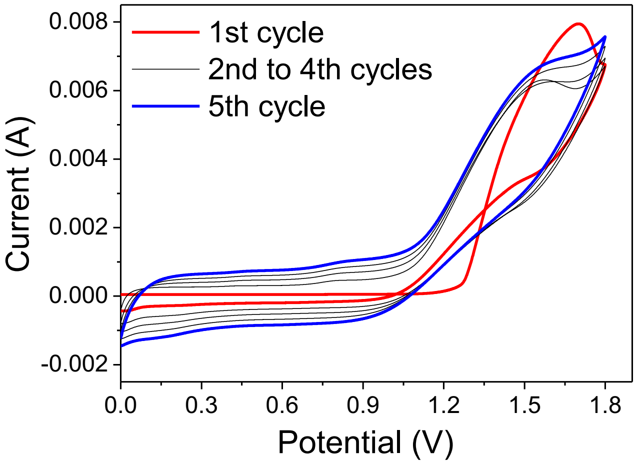


Fig. 1 Repeated cyclic voltammogram of 0.01 M EDOT-Me_2 between 0 and 1.8 V at 100 mV/s for 5 cycles in 0.1 M $LiClO_4$/ACN

2890 cm^{-1} should be due to CH group in the ethylenedioxy bridge; in the low wavenumber range, 1478, 1411, and 1380 cm^{-1} should be due to C=C, C–C in the thiophene ring; 1179 cm^{-1} is corresponding to C–O; and 844 cm^{-1} should be due to C–S in the thiophene ring [14–16].

While the FTIR spectrum of the corresponding polymer PEDOT-Me_2 was comparatively studied, it can be seen in Fig. 2b that, due to the wide chain dispersity of the polymer, the absorption bands were significantly broadened compared with the monomer EDOT-Me_2 [16]. From Fig. 2b it can also be seen that 3110 cm^{-1} absorption band disappeared in the spectrum of the PEDOT-Me_2 implying that the electrochemical polymerization occurred at the 2, 5-positions of the thiophene rings [14–16].

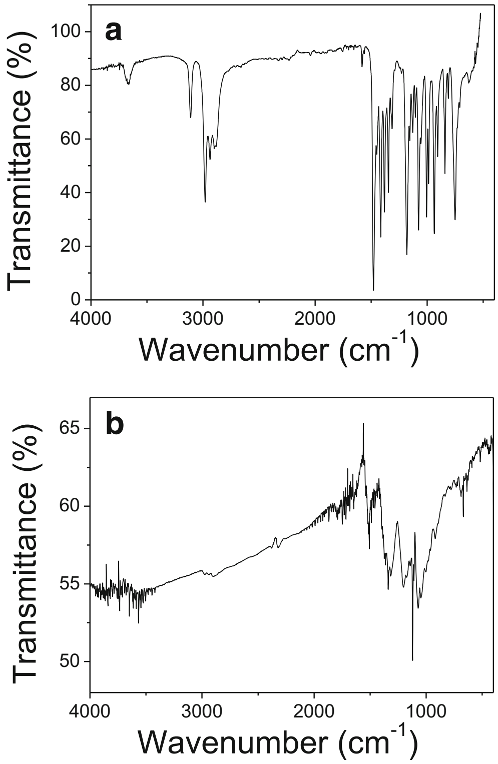


Fig. 2 FTIR spectra of the monomer EDOT-Me_2 (**a**) and the polymer PEDOT-Me_2 (**b**)

Electrochemistry

Figure 3 shows the cyclic voltammetry characterization results of the as-prepared PEDOT-Me_2 film. The CV experiments were performed using a Pt foil (1 cm × 0.4 cm) as the working electrode, a Pt foil (3 cm × 0.7 cm) as the counter electrode, and an Ag wire as the reference electrode in the potential range between − 1.2 and 0.5 V in 0.1 M $LiClO_4$/PC solution which has been selected as the supporting electrolyte as reported by us in the previous studies [17].

From Fig. 3 we can see that PEDOT-Me_2 film shows an oxidation peak at 0.45 V and a reduction peak at − 0.6 V are observed in the redox process.

Spectroelectrochemistry

Spectroelectrochemistry experiment is to check the optical responses of the sample under successively changed externally applied potentials. It is an informative experiment technique in the characterization of electrochromic materials because the optical and electronic properties of the polymer upon redox reaction can be detected simultaneously [18].

It can be seen in Fig. 4 the Vis-NIR absorption spectra of the PEDOT-Me_2 film were characterized under a series of successively changed applied potentials increasing from − 1.2 to 0.5 V. The digital photos of PEDOT-Me_2 film at its neutral state and fully oxidized state are also shown at the bottom of Fig. 4, while Fig. 5 displays the changes of

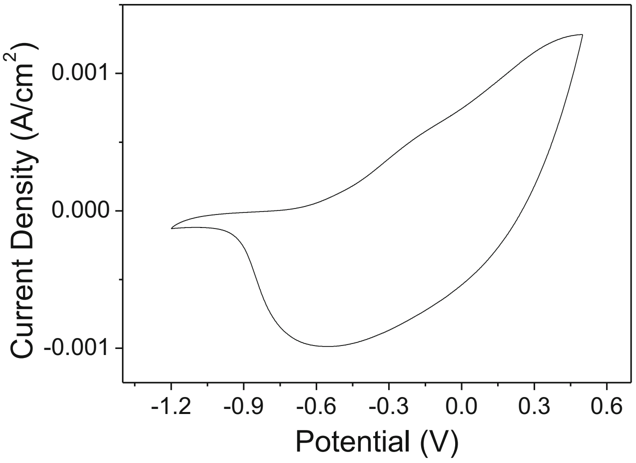


Fig. 3 Cyclic voltammogram of PEDOT-Me_2 film at 100 mV/s in 0.1 M $LiClO_4$/PC using a Pt foil (1 cm × 0.4 cm) as the working electrode, a Pt foil (3 cm × 0.7 cm) as the counter electrode, and an Ag wire as the reference electrode

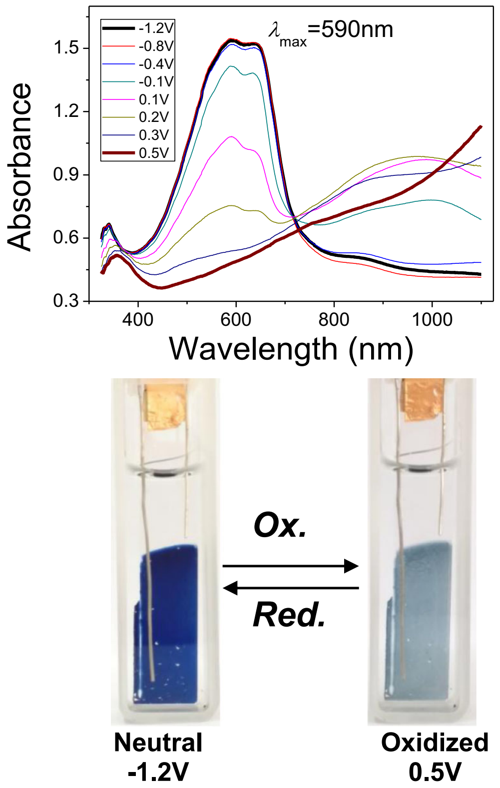


Fig. 4 Spectroelectrochemistry of PEDOT-Me$_2$ film (2 cm × 0.7 cm) at applied potentials from − 1.2 to 0.5 V in 0.1 M LiClO$_4$/PC. Photos at the bottom show the blue neutral state and the transmissive sky blue oxidized state of the polymer film

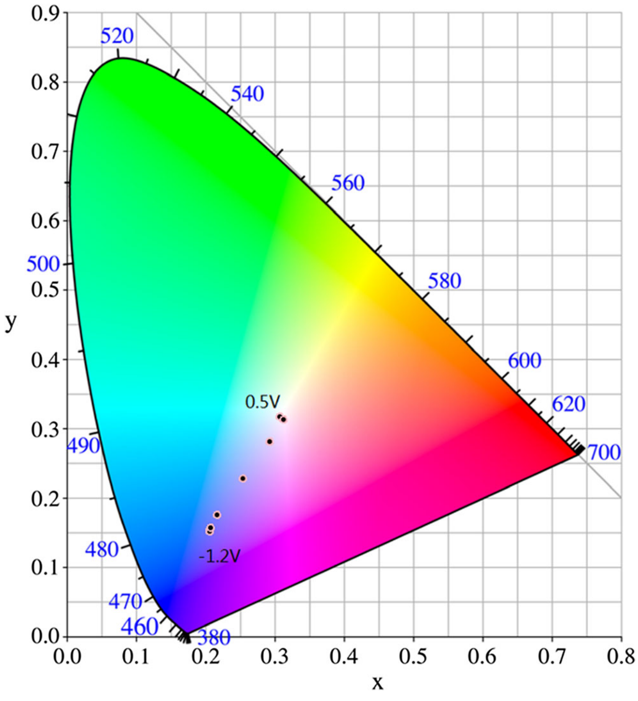


Fig. 5 CIE1931 color coordinates *x, y* of PEDOT-Me$_2$ film at the potentials increasing from − 1.2 to 0.5 V in 0.1 M LiClO$_4$/PC

CIE1931 color coordinates (*x*, *y*) of the PEDOT-Me$_2$ film during the oxidation process from − 1.2 to 0.5 V.

From Fig. 4 we can see that PEDOT-Me$_2$ film has a broad absorption band at 570–650 nm due to the π-m due to the oad absorption band blue neutral state anλ_{max} = 590 nm. A blue color of PEDOT-Me$_2$ film in its neutral form (x = 0.2054, y = 0.1547) is clearly found as indicated in Fig. 4 and corresponding information in Fig. 5. When the potential increased from − 1.2 to 0.5 V, PEDOT-Me$_2$ film is progressively oxidized. The absorption bands at 570–650 nm decrease, and the polymer absorbs at longer wavelength in the near-IR region (> 900 nm) due to the polaronic and bipolaronic transition. Upon fully oxidation (x = 0.3064, y = 0.3170), the intensity of absorption at 570–650 nm decreases significantly and PEDOT-Me$_2$ film shows a transmissive sky blue oxidized state.

Electrochromic switching

The electrochromic switching behavior of PEDOT-Me$_2$ film was studied using square wave potential step chronoabsorptometry and chronocoulometry techniques as shown in Fig. 6a and b. The potential square waves were set as − 1.2 V and 0.5 V with various potential residence time of 10 s, 15 s, and 30s.

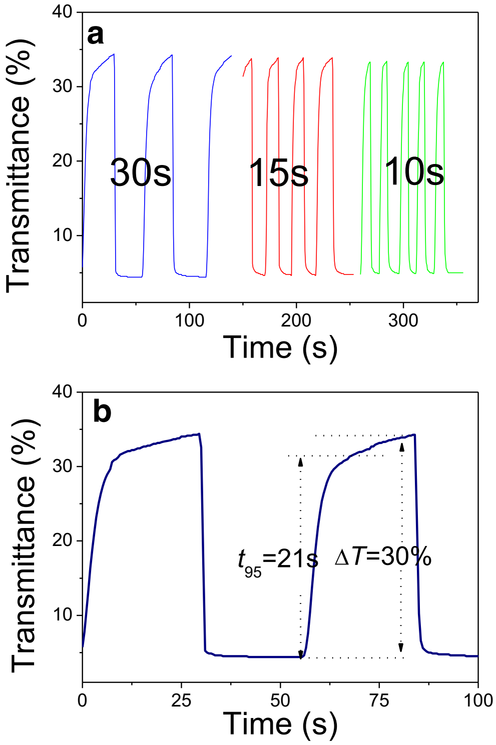


Fig. 6 Square wave potential step chronoabsorptometry at various potential residence time 10 s, 15 s, and 30 s (**a**) and calculation of ΔT and response time (**b**) of PEDOT-Me$_2$ film at 590 nm, − 1.2 to 0.5 V in 0.1 M LiClO$_4$/PC with a Pt wire counter and Ag wire pseudo reference electrode

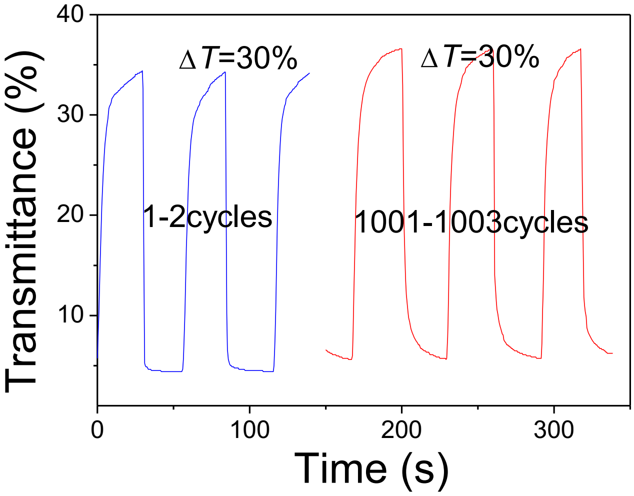


Fig. 7 Square wave potential step chronoabsorptometry of PEDOT-Me_2 film between − 1.2 and 0.5 V in the initial 2 cycles and after 1000 cycles at potential residence time of 30 s in 0.1 M $LiClO_4$/PC

From Fig. 6 we can see that the transmittance of the neutral state and the fully oxidized state are 4.4% and 34.4% at 590 nm respectively. PEDOT-Me_2 film exhibits an improved optical contrast $\Delta T = 30\%$ at 590 nm in comparison with the traditional PEDOT ($\Delta T = 25\%$) [8]. In our point, introducing symmetric methyl groups to the polymer chain will increase the interchain spacing which could facilitate the doping and dedoping processes [17] and therefore improve the optical contrast, i.e., the transmittance change (ΔT) of PEDOT. However the response time of the polymer during the oxidation process is relatively longer (t_{95} = 21 s). It indicates a relatively lower switching speed of PEDOT-Me_2 which could be due to the interaction between methyl pendant groups and the doping ClO_4^- ions.

Long-term switching behavior of an electrochromic film is quite essential for its real-world applications. Total 1000 cycles of square wave potential step chronoabsorptometry scans between − 1.2 and 0.5 V were carried out to check the long-term switching property of the PEDOT-Me_2 film as shown in Fig. 7. In Fig. 7 we can see that, after 1000 cycles, the contrast ratios do not show any loss (ΔT = 30%), indicating that PEDOT-Me_2 has a promising switching stability and could be used in electrochromic applications.

Conclusions

In summary, in this study a novel electrochromic polymer poly(2,3-dimethyl-2,3-dihydrothieno[3,4-b][1,4]dioxine) (PEDOT-Me_2) with symmetrical di-methyl pendant groups was electrochemically synthesized and characterized. The polymer exhibits promising electrochromic nature and displays a blue neutral state and a transmissive sky blue oxidized state. It has a reasonable improved optical contrast of 30% at 590 nm compared with the traditional electrochromic polymer PEDOT, but a relative longer switching time t_{95} = 21 s during the bleaching process and good long-term switching stability.

Funding information This work received financial support from Anhui Natural Science Foundation (1808085 MB29); Natural Science Foundation of Anhui Jianzhu University (JZ182011); Anhui Province College Natural Science Foundation (KJ2017A482); The Support Plan Project of Excellent Young Talents in Universities in Anhui Province (gxyq2017023); The Open Foundation of Anhui Province Key Laboratory of Advanced Building Materials of Anhui Jianzhu University (JZCL201602ZZ); College Students Innovation and Entrepreneurship Training Plan Project (201910878000).

References

1. Beaujuge PM, Reynolds JR (2010) Chem Rev 110(1):268–320
2. Gunbas G, Toppare L (2012) Chem Commun 48(8):1083–1101
3. Neo WT, Ye Q, Chua S, Xu J (2016) J Mater Chem C 4(31):7364–7376
4. Lv X, Li W, Ouyang M, Zhang Y, Wright DS, Zhang C (2017) J Mater Chem C 5(1):12–28
5. Beverina L, Pagani GA, Sassi M (2014) Chem Commun 50(41):5413–5430
6. Amb CM, Dyer AL, Reynolds JR (2011) Chem Mater 23(3):397–415
7. Chen X, Liu H, Xu Z, Mi S, Zheng J, Xu C (2015) ACS Appl Mater Interfaces 7(21):11387–11392
8. Meng J, Li X, Qin M, Pei Y, Yang S, Lan Y, Wang R, Chen G (2017) Org Electron 50:16–24
9. Welsh DM, Kumar A, Meijer EW, Reynolds JR (1999) Adv Mater 11(16):1379–1382
10. Chen X, Yang M, Xu W, Qu Q, Zhao Q, Zou W (2019) J Solid State Electrochem 23(1):19–25
11. Chen X, Zhang J, Yang M (2018) J Mater Sci: Mater Electron 29:16469–16477
12. Chen X, Qu Q (2018) Sol Energy Mater Sol Cells 179:270–275
13. Chen X, Yang M, Qu Q, Zhao Q, Zou W (2018) J Electroanal Chem 820:60–66
14. Soganci T, Gumusay O, Soyleyici HC, Ak M (2018) Polymer 134:187–195
15. Carbas BB, Kivrak A, Onal AM (2011) Electrochim Acta 58:223–230
16. Zhang S, Xu J, Lu B, Qin L, Zhang L, Zhen S, Mo D (2014) J Polym Sci, Part A: Polym Chem 52(14):1989–1999
17. Chen X, Xu Z, Mi S, Zheng J, Xu C (2015) New J Chem 39(7):5389–5394
18. Zhai Y, Zhu Z, Zhou S, Zhu C, Dong S (2018) Nanoscale 10(7):3089–3111