Flexible Electrochromic Poly(thiophene-furan) Film via Electrodeposition with High Stability

Wen-Qian Yao, Pei-Pei Liu, Wei-Qiang Zhou, Xue-Min Duan, Jing-Kun Xu*, Jia-Ji Yang, Shou-Li Ming, Meng Li, and Feng-Xing Jiang*

Flexible Electronics Innovation Institute, Jiangxi Science and Technology Normal University, Nanchang 330013, China

Abstract Flexible electrochromic (EC) materials have an urgent demand in the current electronic equipment market due to their technological interest and applications. However, at present, few flexible EC devices developed by industry exist due to some problems and challenges still to be solved such as flexibility. In this work, we have successfully synthesized a novel thiophene-furan (TFu) monomer via Stille coupling reaction, and facilely electrochemically polymerized in a neutral Bu₄NPF₆·CH₃Cl₂ electrolyte system to afford the corresponding poly(thiophene-furan) (PTFu) polymer film with good flexibility. The electrochemical and photoelectrochemical analyses of the as-prepared PTFu demonstrate that it has achieved the improved EC performance compared with pure polyfuran and polythiophene polymers, and as a result it possesses favorable EC parameters manifested as a reasonable ΔΔT (32.1%), faster response (1.38 s), excellent coloration efficiency (CE, 300.9 cm²-C⁻¹), and after a continuous redox process up to 2000 s, its optical stability can be maintained at 96%, and even after 3000 s, it can still be maintained at 80%. In addition, the successful assembly of the electrochromic device of PTFu film can easily realize the reversible conversion of the color from orange to gray. All these systematic studies suggest that the as-prepared flexible PTFu film is a promising candidate for EC materials and has great potential interest for versatile EC applications.

Keywords Organic conjugated polymers; Polyfuran derivatives; Electrochromism; Flexibility; Electrochromic devices

Citation: Yao, W. Q.; Liu, P. P.; Zhou, W. Q.; Duan, X. M.; Xu, J. K.; Yang, J. J.; Ming, S. L.; Li, M.; Jiang, F. X. Flexible electrochromic poly(thiophene-furan) film via electrodeposition with high stability. Chinese J. Polym. Sci. 2021, 39, 344–354.

INTRODUCTION

Electrochromic (EC) materials are broadly defined as those display reversible optical changes accompanied with reversible color changes under the externally applied voltage. In an era of actively advocating and responding to low-carbon energy sources, the research and application of EC materials as clean energy sources have become quite significant. So far, in-depth research on EC materials has made considerable progress. The EC materials initially studied are inorganic semiconductors represented by tungsten trioxide (WO₃)¹ and nickel oxide (NiO)² and other transition metal complexes (such as Prussian blue),³ and then organic small molecules (such as viologens).⁴ Conductive polymers (CPs), as the third generation EC materials, have been widely concerned due to their excellent properties, such as easy processing, easy multi-colorization via structural adjustments, high optical contrast ratio, and fast switching rates.⁵ EC materials have been successfully commercialized as electrochromic devices (ECDs) in smart windows, electronic papers, smart mirrors, and EC display devices. However, ECDs are still facing challenges such as low flexibility, poor durability etc., which severely limits their active life and applications.⁶

To date, many efforts have focused on the research of EC materials and the use of multiple strategies to exploit CPs with excellent flexibility and EC performance. These diversified strategies currently employed in most researches include designing a molecular structure composed of alternating combinations of donor units and acceptor units on the polymer backbone, changing asymmetric structures or different pairs of side chain lengths of CPs by using copolymerization to illuminate the relationship between structure and performance of the polymer. By tailoring polymer molecular structure to adjust band gap, the EC performance of polymer materials can be further significantly optimized.

As a typical five-membered unsaturated heterocyclic conductive polymer, polythiophene (PTh) possessing unique optical, electrical characteristics and prominent environmental stability has been widely concerned in recent years due to the fact that its molecular structure can be easily tailored to optimize the electronic properties, and thus has an important research prospect in the field of EC materials.⁷ However, the
homologous polyfuran (PFu) has been less studied in recent years, which is attributed to the drastic polymerization conditions. Generally, the conventional polymerization methods including chemistry and electrochemistry always lead to the poor performance of PFu polymers, such as poor flexibility and low stability.\[9] It is worth noting that furan is considered as an important green organic energy material since it can be produced from the cracking process of rice hulls and has good biodegradability. Furthermore, it has excellent solubility and potential EC performance, so the EC properties based on PFu and its derivatives were investigated and they were found to exhibit quasi-reversible redox behavior accompanied with a reversible EC behavior, but they all face the low transmittance and the poor optical stability.\[9] Our group studied the EC properties of a series of PFu films, and the results show that these polymers all have poor EC performance, which is an expected result since the obtained PFu films have weak electrochemical stability, and we then conducted research in an attempt to introduce stable EDDT building block into furan-based monomers, in order to enhance the stability and EC properties.\[10] Kavak’s group adopted a similar strategy and finally got a furan derivative material with the better EC properties.\[11] It is worth noting that the addition of furan unit structure to CPs leads to high performance materials.\[11−13] Inspired by the strategy, we synthesized a simple novel monomer 2-(thiophen-2-yl) furan (TFu) containing thiophene and furan unit linked by Stille coupling method. The embedding of furan building blocks not only improves the solubility of TFu monomer, but also increases the effective conjugate length of the monomer and the delocalization possibilities of the derived radical cations, which is conducive to better polymer performance.\[13,14] It is expected that PTFu has both the excellent properties of PFu and PTh and significant EC properties.

In this work, the TFu monomer was synthesized by Stille coupling method, and characterized by 1H-NMR. The corresponding electropolymerized high-quality PTFu film obtained in a neutral system is shown in Fig. 1, which possesses the quasi-reversible properties, electrochemical stability and intriguing EC properties. Structural characterization, scanning electron microscopy (SEM), electrochemistry, spectrotroelectrochemistry, and EC performances of the obtained polymers were also investigated. The systematic research shows that PTFu film is a promising organic EC material in the field of flexible EC materials.

**EXPERIMENTAL**

**Chemicals**

Furan (Fu, 99%+) and thiophene (Th, 99%) were purchased from Damas-beta and Shanghai J&K Scientific Ltd., respectively, and then used after distillation under nitrogen atmosphere. 2-Bromo-furan (99%), 2-(tributylstanny)thiophene (99%), tetrakis(triphenylphosphine)palladium(0) and boron trifluoride diethyl etherate (BFE, 48% BF3) were bought from Aldrich Chemistry and were used directly. Dichloromethane (CH2Cl2, >99% J&K Seal) needs to be distilled in nitrogen atmosphere using calcium hydride for 6 h. Tetrabutylammonium hexafluorophosphate (Bu4NPF6, 98%; Energy Chemistry) was vacuum dried before use.

**Electrochemical Experiments**

Electrochemical measurements including the electropolymerization of the monomers and the electrochemical performance of the polymers were implemented in a three electrodes cell with the use of Princeton V3 controlled by a computer. The electrode cell consists of two Pt wires and one Ag/AgCl electrode, which was calibrated with a saturated calomel electrode used as working electrode, counter electrode, and reference electrode, respectively. These films used for testing were electropolymerized on indium tin oxide (ITO) glass by a potentiostatic method. Finally, these newly prepared films were rinsed with CH2Cl2 for the next test.

**Electrochromic Performance Measurements**

Both spectroelectrochemical and kinetic studies were actualized on a Princeton V3 potentiostat-galvanostat and a Cary 50 UV/Vis/NIR spectrophotometer controlled by a computer. Spectral electrochemical cell is composed of quartz cell, polymer adsorbed ITO glass, Pt wire and Ag/AgCl electrode. All tests were performed in CH3Cl2-Bu4NPF6 (0.1 mol·L−1). The subtraction operation was performed on the background of the CH3Cl2-Bu4NPF6 electrolyte solution and the ITO glass before the experiments.

**Characterization Method**

1H-NMR spectra of monomer were recorded on a Bruker AV400NMR spectrometer using DMSO as the solvent. FTIR spectroscopy of film with KBr pellets was performed using an IRTTracer-100 FTIR spectrometer over the range from 300 cm−1 to 4000 cm−1. Thermogravimetric analysis (TGA) was carried out by a TGA Q500 thermal analyzer at room temperature in nitrogen atmosphere. Scanning electron microscopy (SEM) was implemented to characterize the microstructure of the polymers polymerized in CH3Cl2-Bu4NPF6/BFE electrolyte system deposited on the ITO with SUPRA 55 Instrument, and all theoretical calculations were carried out using the Gaussian 03 program.

**Electrochromic Devices (ECDs) Assembly**

The ECDs were mainly composed of the following three parts, that is, the gel electrolyte coated on the newly prepared PTFu film attached to the ITO glass substrate, and tightly clamped by the ITO glass substrate as the counter electrode. Finally, the device was air-tightly encapsulated with copper foil and epoxy-resin glue. The gel electrolyte was prepared by adding Bu4NPF6 (0.34 g) and hydrated poly(methyl methacrylate) (PMMA) (1.30 g) into a three-neck flask and dissolved in CH3Cl2 (17 mL) with stirring, followed by vigorous stirring at 60–65 °C for 12 h. Finally, the transparent PMMA-based gel electrolyte was obtained.
RESULTS AND DISCUSSION

Electrochemical polymerization is generally considered to be an efficient polymerization method for the preparation of polymer materials with excellent properties. Here we systematically investigated the electrochemical behavior of TFu and PTFu in the Bu₄NPF₆-CH₂Cl₂ (0.1 mol·L⁻¹) electrolyte system, and compared them in detail with the corresponding properties of PTh and PFu. TFu presents the initial oxidation potential at 1.0 V versus Ag/AgCl in the first scan in Fig. 2(a), indicating the formation of TFu radical cations, which may induce to the supply of desirable organic polymer films, and significant increments of current density suggest the smooth formation of electroactive polymers. Therefore, a free-standing flexible PTFu film can be easily obtained and stripped from the ITO glass. Organic polymer films with the above-mentioned excellent quality properties are ideal candidates since they have strong mechanical properties, which will be beneficial to the application of organic electronic device such as EC materials. In addition, the characteristic band of FTIR spectrum further proves the formation of PTFu and its good thermal stability is proved through TGA mea-

Fig. 2  Cyclic voltammograms of (a) TFu (0.01 mol·L⁻¹), (b) Fu (0.01 mol·L⁻¹) and (c) Th (0.01 mol·L⁻¹) in CH₂Cl₂-Bu₄NPF₆ (0.1 mol·L⁻¹) at a scan rate of 50 mV·s⁻¹; CVs of (d) PTFu, (e) PFu and (f) PTh films in monomer-free CH₂Cl₂-Bu₄NPF₆ (0.1 mol·L⁻¹) at different scan rates from 25 mV·s⁻¹ to 300 mV·s⁻¹ (Inset: digital image of free-standing PTFu film peeled from ITO).
measurements (see Fig. S2 in the electronic supplementary information, ESI). On the other hand, in comparison with TFu monomer, furan (Fu) and thiophene (Th) exhibit the higher onset oxidation potential in the same electrolyte solutions as above and thus fail to produce high-quality polymer films (Figs. 2b and 2c), which is consistent with previous reports (see Fig. S3 in ESI).\textsuperscript{[17]} Therefore, the results of these electrochemical experiments declare that the introduction of the electron-donating thiophene group at the active sites of the TFu unit allows the formation of an excellent polymer film.\textsuperscript{[18]}

PTFu cyclic voltammetry (CV) curves were tested in a monomer-free Bu$_4$NPF$_6$-CH$_2$Cl$_2$ electrolyte system to explore their electrochemical activity as shown in Fig. 2(d). The CV curves of PTFu film reveal a quasi-reversible redox behavior with a clear couple of peaks at a scan rate from 25 mV·s$^{-1}$ to 300 mV·s$^{-1}$, implying the good electrochemical activity and reversible properties. As expected, PTFu film exhibits fairly good reversibility as against PTu and PTh in Bu$_4$NPF$_6$-CH$_2$Cl$_2$ neutral system, which confirms the chemical structure of the monomer and the electrolyte system have a crucial effect on the result of electrochemical polymerization.

**Fig. 3** Electrochemical stability of (a) PTFu, (c) PTh, and (e) PFu films in monomer-free CH$_2$Cl$_2$-Bu$_4$NPF$_6$ (0.1 mol·L$^{-1}$) at the potential scan rate of 100 mV·s$^{-1}$. (b, d, f) Plots of redox peak current densities versus potential scan rates. $j_p$ is the peak current density, and $j_{p,a}$ and $j_{p,c}$ denote the anodic and cathodic peak current densities, respectively.
It is well known that a CP with excellent stability is one of the utmost essential requirement for practical applications of electronic devices, and thus we further explored the electrochemical stability of PTFu polymer film in monomer-free Bu$_4$NPF$_6$-CH$_2$Cl$_2$ system at the scanning rate of 0.15 V s$^{-1}$, as shown in Fig. 3. It should be kept in mind that the electrochemical stability monitoring of PTFu was performed under ambient conditions. After 100 CV cycles for a wider potential window (from 0 V to 1.1 V), PTFu film still retains 84% of its original electrochemical activity, in contrast to the electrochemical stability of 50 cycles of PFu (67%) and 100 cycles of PTh (63%), respectively, and it is even better than PFu and PTh films obtained in BFFE solution (see Fig. S4 in ESI)[17,19]. Besides, it can be clearly observed from Fig. 3(b) that the peak current density of the redox peaks of the PTFu film reveals an excellent linearly proportional relationship with the scan rate ($R^2=0.9993$ and $R^2=0.9998$ for anodic and cathodic fitting, respectively), indicating that the electrochemical process of PTFu is a non-diffusive redox process, and the high-quality film can be well attached to the Pt electrode surface[20]. However, in the case of the PTh and PFu films deposited from Bu$_4$NPF$_6$-CH$_2$Cl$_2$ or BFFE electrolyte systems, they both revealed lower regression coefficients as can be seen from Figs. 3(d) and 3(e) and Fig. S4 (in ESI).

Electrochemical impedance spectroscopy (EIS) was performed to investigate the electrochemical behavior of the polymer film with a frequency range of 0.01 Hz–100 kHz. It is observed from the Nyquist plots (Fig. 4) that the PTFu film displays a vertical shape compared to PTh and PFu films electrochemically deposited in the CH$_2$Cl$_2$-Bu$_4$NPF$_6$ electrolyte system in the low frequency region, suggesting lower ion transfer resistance in the PTFu material[21]. In the high frequency domain (inset), the intercept of the plot with the real axis represents solution resistance ($R_s$). The $R_s$ values of PTFu, PTh and PFu are arranged as follows, 279 Ω (PTFu) < 324 Ω (PTh) < 324 Ω (PFu), suggesting that the PTFu film has a smaller resistance with good ion response than PTh and PFu film. The size of the semicircle is determined by the charge transfer resistance ($R_t$) at the interface between the electrode material and the electrolyte, which were determined from the diameters of the semicircles. The $R_t$ values of PTFu can be ignored, while PTh and PFu exhibit the large $R_t$ values. This means that both the electron transport and the charge transfer resistance of the PTFu films are lower than those of the PTh and the PFu film, which is attributed to the low charge transfer resistance and fast electron transfer of PTFu at the electrode/electrolyte interface and reflects the formation of active PTFu polymer, consistent with its favorable electrochromic results.

The excellent electrochemical behavior of PTFu mentioned above in neutral system is mainly rooted in the following two aspects: (a) the increase of the effective conjugate length of the TFu monomer facilitates the successful electrochemical polymerization of PTFu films with excellent redox properties and (b) the embedding of the thiophene building block with excellent stability in the monomer significantly improves the electrochemical stability of the film, which imply that PTFu is an EC material candidate with better EC characteristics and long-term switching ability in Bu$_4$NPF$_6$-CH$_2$Cl$_2$ electrolyte system, and it is consistent with the conclusions in the following section on EC performance.

Quantum chemical calculation can effectively explicate the mechanism of polymerization and help to understand the structure of monomers and corresponding polymers[22]. Therefore, in order to deeply understand the relationship between molecular structure and properties of polymers, the ground-state geometry optimizations and energy levels of PTFu, PTh, and PFu are optimized by using density functional theory (DFT) calculations at B3LYP/6-31G level, and the corresponding theoretical band gaps are calculated. The optimized geometry and the wave functions of PTFu, PTh and PFu polymer films are depicted in Fig. 5. As can be observed, these polymers have good planarity and a twist angle of almost 0° as expected, which is one of the consensuses of PFu and its derivatives[18]. The perfect planarity is beneficial to en-

![Fig. 4 Nyquist plots of PTFu, PTh and PFu films of electrochemical potentiostatic polymerization in CH$_2$Cl$_2$-Bu$_4$NPF$_6$ electrolyte system.](https://doi.org/10.1007/s10118-021-2501-7)
hancing the \( n\pi \) interactions between adjacent backbones of the polymer, thereby further promoting the migration of the interchain carriers.\[^{23}\] It can be easily seen that the HOMO and LUMO orbitals of these polymers have similar electron cloud distributions, that is, they are well-distributed delocalized on the HOMO and LUMO orbitals of the backbones of these polymers, which can facilitate intramolecular charge transport.\[^{29}\] Compared to PFu (−4.92 eV) and PTh (−5.15 eV), PTFu film has a higher HOMO (−4.67 eV) level, which can be attributed to the introduction of thiophene with electron-rich characteristics,\[^{24}\] resulting in longer polymer backbone lengths and lower \( E_g \) (2.74 eV). The higher HOMO level means that PTFu is more susceptible to oxidation, which may result in a fast color conversion rate,\[^{25}\] and this advantage is of significance for the application of EC materials.

The microstructure and stacking mode of polymer play a key role in its properties\[^{26}\] and a great deal of research has confirmed that the conductivity, electron transfer speed and stability of polymer materials are largely related to these microscopic features.\[^{27}\] Scanning electron microscopy (SEM) is a common method for characterizing polymer morphology and the SEM images of PTFu, PTh and PFu films obtained by electrochemical polymerization in different electrolyte systems are shown in Fig. 6. It can be seen from the images that the microscopic morphology of these films is composed of uniformly well-distributed microspheres, which means that they have a larger specific surface area, which is beneficial to the increase of contact area between the polymer and the electrolyte solution. It will help to speed up the free flow of the ion carrier into and out of the film, and improve the EC efficiency of the polymer, including response time, coloring efficiency, etc. Compared with PTh and PFu deposited in BFEE solution, PTFu prepared in neutral system has a large specific surface area, which confirms the prospect of application of PTFu film in the field of EC materials.

Spectroelectrochemistry is a common measurement method, which can be used to obtain the absorption spectrum of organic conjugated polymer materials under different applied voltages and the change information of electronic polymer structure.\[^{28}\] To observe completely detailed changes in optical behavior, polymer films deposited on ITO glass were spectrally measured by raising the potential from neutral to oxidized state in Bu\(_4\)NPF\(_6\)-Bu\(_4\)Cl electrolyte system. The absorption spectra of the prepared PTFu, PTh and PFu films controlled by different potentials are shown in Fig. 7. PTFu film exhibits a single strong absorption peak at 440 nm in its neutral form (−0.2 V) presented as Fig. 7(a), which may be attributed to \( n\pi^* \) transitions.\[^{29}\] As the applied potential became more anodic, the evolution of the spectra presents a gradually decreased intensity of the neutral band, accompanied by the appearance of two new absorption bands at 725 and 1030 nm, respectively, indicating the formation of corresponding polarons and double polarons.\[^{30}\] Simultaneously, the color of the PTFu film underwent a significant change in the redox process, that is, the polymer revealed multi-colored behaviors, showing color changes from orange-red (−0.2 V) to brown (0.1 V) to tan (0.3 V) to dark gray (0.8 V) from the inset image. However, the above-mentioned poor electrochemical behaviors of PTh and PFu under the same electrochemical condition resulted in almost no regular spectral curve changes or obvious color conversion during the test, which is similar to previously reported results.\[^{31}\] In addition, the band gaps of these polymer films were calculated by onset of light absorption and all the results are summarized in Table 1. It can be analyzed from these data that the PTFu film polymerized in Bu\(_4\)NPF\(_6\)-CH\(_2\)Cl\(_2\) has a smaller band gap (1.94 eV) due to the increase in backbone conjugation length. Nevertheless, PFu and PTh polymer have larger band gaps in both Bu\(_4\)NPF\(_6\)-CH\(_2\)Cl\(_2\) and BFEE polymerization systems, which is related to the poorer conjugated level of films compared to PTFu film.\[^{32}\] In fact, polymers with low band gap can be easily implemented at lower potentials to achieve multiple changes in color, which is beneficial to improving EC performance.

CPs as the active layer of ECDs are of great significance in the field of organic electronic materials over the past decades. To elucidate the EC performance of PTFu film, its parameters were analyzed, including response time, optical contrast (\( \Delta T \) %), coloration efficiency (CE), and optical stability, and these parameters are the decisive criteria for measuring the performance of EC materials. Kinetic studies were executed by a double-step chronoamperometry technique coupled with a UV spectrophotometer to elucidate the EC parameters for the PTFu films. The transmittance changes as a
of time were monitored with a square-wave potential step method between reduction (−0.2 V) and oxidized states (0.8 V) with a time interval of 10 s at its maximum absorption wavelength in a monomer-free Bu$_4$NPF$_6$/CH$_2$Cl$_2$ (0.1 mol·L$^{-1}$) electrolyte system in Fig. 7 and Table 2. As can be seen from the transmittance-time profiles of PTFu film shown in Fig. 7(d), PTFu film possesses reasonable optical contrast in the redox process with 678 nm of 31.6% and 430 nm of 12.8% in the visible region. Based on analysis of polymer film transmittance-time curves, the PTFu switches between neutral and oxidation states quickly, and the response time was calculated as 1.38 and 1.86 s, indicating the fast ion transport in PTFu chains in the redox process.$^{[33]}$ The switching time shown above is significantly shorter than the switching time (2 s) of typical switching time for EC polymer films.

Coloration efficiency (CE) is an effective tool for measuring the power requirements of EC materials based on the transmittance-time profiles analysis. The CE is defined as the relation between the injected/ejected charge as a function of electrode area ($Q_d$) and the change in optical density ($\Delta OD$) at...
The decrease in stability here may be related to the degradation of PTFu material caused by long-term repeated switching. The optical properties of PTFu film, and evaporation of the electrolyte, and PTFu and PTh films prepared in the BFEE solution under the promising long-term optical stability even compared with new prepared PTFu film deposited on ITO glass has been subjected to a spectroelectrochemical test for up to 3000 s at its maximum absorption wavelength in air atmosphere to study its long-term optical stability. Compared with stable optical stability of 2000 s (96%), the stability of the PTFu film after 3000 s has been slightly reduced and maintained at 80%.

Stability is an important indicator of the guaranteed EC fundamental property, so square-wave potential step absorbimetry was used to expound the long-term switching stability of PTFu deposited on the ITO glass in a monomer-free Bu4NPF6-CH2Cl2 electrolyte system. Fig. 8(a) shows the measured transmission-time profiles of PTFu film at 430 and 678 nm in the redox process (−0.2 V to 0.8 V), respectively. After up to 2000 s of repeated switching between oxidized and reduced states, the value of $\Delta T$ at 678 nm held at 30.3% without any significant decline compared with its initial state ($\Delta T=31.6\%$), that is, its $\Delta T$ stability can still be maintained at 96% after a long redox process. Meanwhile, similar exhilarating result was obtained in long-term optical stability experiments at 430 nm. The results demonstrated that PTFu has promising long-term optical stability even compared with PTh and PFu films prepared in the BFEE solution under the same test conditions (Figs. 8b and 8c), which was in good agreement with the electrochemical stability results discussed above. Importantly, a high-quality organic polymer film requires stable redox process for its electrochromic properties to be reproducible upon repeated switching, so the newly prepared PTFu film deposited on ITO glass has been subjected to a spectroelectrochemical test for up to 3000 s at its maximum absorption wavelength in air atmosphere to study its long-term optical stability.

### Table 1
Optical properties and theoretical calculation data of PTFu, PTh and PFu films.

| Polymer | Electrolyte system | $\lambda$ (nm) | $\Delta T$ (%) | $\tau$ (s) | Optical stability (%) (2000 s) |
|---------|--------------------|----------------|--------------|-----------|-----------------------------|
| PTFu    | CH2Cl2-Bu4NPF6     | 430            | 12.8         | 1.9       | 166.0 (1200 s)             |
|         |                    | 678            | 31.6         | 1.8       | 300.4                       |
|         | BFEE               | 423            | 1.3          | 4.8       | 7.9                         |
|         |                    | 678            |             |           | 33.6 (1200 s)              |
| PTh     | CH2Cl2-Bu4NPF6     | 669            | 8.1          | 1.6       | 1.9                         |
|         | BFEE               | 782            |             |           |                             |
|         |                    | 669            | 20.1         | 2.9       | 188.6                       |
|         | BFEE               | 733            | 37.4         | 1.4       | 119.2                       |
| PFu     | CH2Cl2-Bu4NPF6     | 488            |             |           |                             |
|         | BFEE               | 374            | 4.9          | 1.7       | 27.9                        |
|         |                    | 607            | 14.3         | 2.2       | 103.0                       |

### Table 2
Electrochromic parameters of the prepared films at their maximum absorption wavelength in two electrolyte systems.

| Polymer | Electrolyte system | $\lambda_{\text{onset}}$ (nm) | $E_g^b$ (eV) | HOMO $^b$ (eV) | LUMO $^b$ (eV) | $E^b$ (eV) |
|---------|--------------------|-------------------------------|-------------|--------------|----------------|-----------|
| PTFu    | Bu4NPF6-CH2Cl2    | 639                           | 1.94        | −4.67        | −1.93          | 2.74      |
|         | BFEE               | 606                           | 2.04        |              |                |           |
| PTh     | Bu4NPF6-CH2Cl2    | 668                           | 1.85        | −5.15        | −1.71          | 3.44      |
|         | BFEE               | 628                           | 1.98        |              |                |           |
| PFu     | Bu4NPF6-CH2Cl2    | 488                           | 2.54        | −4.92        | −1.07          | 3.85      |
|         | BFEE               | 573                           | 2.17        |              |                |           |

*Calculated by the following formula: $1240/\lambda_{\text{onset}}$. *b* Measured by using density functional theory (DFT) calculations at B3LYP/6-31G lev.

The specific dominant wavelength ($\lambda_{\text{onset}}$) of the sample as illustrated by the following equation: $\text{CE} = \text{ODD} / Q_d$ (1)

where $\Delta \text{OD} = \log(T_{\text{ox}}/T_{\text{red}})$, $T_{\text{ox}}$ and $T_{\text{red}}$ are the transmittance of polymer at oxidized and neutral states, respectively. $Q_d$ is the density of injected/ejected charge during the change of polymer between oxidized and neutral states. Here the calculated CE values of PTFu film were 165.95 cm$^2$·C$^{-1}$ at 430 nm and 300.9 cm$^2$·C$^{-1}$ at 678 nm, which benefit from the unique EC properties of PTFu film.
polymer can still be considered as an organic material with favorable long-term optical stability. In addition, the research results of PTh, PFu and their derivatives in the field of EC materials in recent years are summarized in Table S1 (in ESI). It can be concluded that PFu possesses the prominent EC performances, which are reflected as superior CE values, improved response time, higher ΔT (%) and excellent stability. The systematic EC experiments conducted on the PFu film indicate that the introduction of stable thiophene units into the furan-based structure leads to the polymerization of high-quality PFu film with unique EC behavior in neutral electrolyte systems.

The development of flexible, lightweight, low power consumption ECDs is the need of the hour for an intelligent environment. CPs are a class of major materials that exhibit potentially flexible EC properties as films, such as PEDOT, polyaniline, and benzodithiazole. As discussed above, these conclusions indicate that PFu film has unique EC performance, so a typical sandwich ECD was assembled based on these conclusions. The type of the ECD was assembled in a manner of glass/PMMA-Bu4NPF6/PFU/ITO glass, where the EC layer was PFu that served as a working electrode, an ITO grass was used as the counter electrode, and poly(methyl methacrylate) (PMMA) and Bu4NPF6-CH3Cl2 combined as gel electrolyte tightly encapsulated the two electrodes to complete the assembly of the device. The process of ECD’s performance monitoring was the same as described above. As a result, the color of PFu films used as working electrodes in both devices can achieve a reversible transition from oxidation state (0.8 V) to reduction state (−0.2 V), indicating that the newly prepared device has favorable redox performance and is one of the successfully assembled ECDs. At present, ECD assembled with PFu film deposited on ITO elastic substrate cannot be bent to a greater extent, and subsequent work will focus on increasing the elasticity of ECDs. In recent years, it has been reported that the EC properties of PTh and PFu derivatives have been widely investigated. However, these results are almost related to the EC performance of these materials and there are few reports on ECD assembly. Here we report the ECD assembly of PFu organic polymers, expecting that polymers with this structure will provide a sensible way for further study of novel EC materials and ECD assembly.

**CONCLUSIONS**

We have successfully obtained novel TFu monomer with excellent solubility through Stille coupling reaction, and then the corresponding high-quality free-standing PFu film was obtained by electropolymerization in neutral system. The electrochemical and photoelectrochemical analyses of the polymer demonstrated that PFu film possesses the outstanding electrochemical and photoelectrochemical stability performance. As a result, the PFu film has excellent EC properties, manifested as a reasonable ΔT (32.1 %), faster response (1.38 s), excellent CE (300.9 cm²C⁻¹), and prominent optical stability. Moreover, we successfully achieved the assembly of ECDs based on PFu film. The excellent EC behavior of PFu is mainly attributed to the embedding of the thiophene building block with excellent stability, which increases the effective conjugate length of the TFu monomer and is conducive to the preparation of high-quality film. The systematic study indicates that the furan-based molecular structure and EC properties of PFu polymer will provide a powerful a reference angle for the development and application of EC materials.

![Flexible PTFu film](https://doi.org/10.1007/s10118-021-2501-7)

**Electronic Supplementary Information**

Electronic supplementary information (ESI) is available free of charge in the online version of this article at http://dx.doi.org/10.1007/s10118-021-2501-7.

**ACKNOWLEDGMENTS**

This work was financially supported by the National Natural Science Foundation of China (Nos. 51762018 and 51863009), the Natural Science Foundation of Jiangxi Province (Nos. 20165BCB18016, 20181ACB20010, and 20202ACBL204005), and Jiangxi Provincial Department of Education (Nos. GJJ190584 and GJJ190612).

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