Fluorinated oleophilic electrochromic copolymer based on 3-(N-trifluoroacetamido)thiophene and 3,4-Ethylenedioxythiophene EDOT

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Abstract: A new fluorine-containing monomer 3-(N-trifluoroacetamido)thiophene (**F-TH**) was synthesized and characterized for the first time. Its molecular structure was determined by a single-crystal X-ray study. **F-TH** functions as a building block in electropolymerization with 3,4-ethylenedioxythiophene (**EDOT**) gives a novel conjugated copolymer **P(F-TH:EDOT)** subsequently. Compared with the parent homopolymer poly(3,4-ethylenedioxythiophene) (**PEDOT**) film, sponge-like nanoporous **P(F-TH:EDOT)** film has a slightly larger band gap with a reduced hydrophilic and increased oleophilic surface. Spectroelectrochemical analysis results reveal that **P(F-TH:EDOT)** exhibits excellent electrochromic performances with higher optical contrast (55%) and much shorter coloring time (0.70 s) than that of **PEDOT** (43%, 1.54 s). The coloration efficiency value of **P(F-TH:EDOT)** achieves up to 167.9 cm²/C, 55% higher than that of **PEDOT** (108.1 cm²/C). These improved electrochromic properties of **P(F-TH:EDOT)** are probably related with the enhanced wettability to electrolyte solution.

Electrochromic conjugated polymers (**ECPs**), which can effectively adjust the transmitted and reflected light based on their reversible redox states under small external voltages, have been extensively investigated owing to their potential applications on smart windows and mirrors, displays, thermal control, camouflage and sensors.¹⁻⁸ As the most established **ECPs**, thiophene-based polymers have been extensively investigated due to their significant optical changes between redox states, outstanding coloration efficiency and facile switching performances.⁹⁻¹² To date, a lot of monomers from the family of thiophenes have been developed as building blocks, and based on them, various **ECPs** with different properties have been synthesized,¹³⁻¹⁸ but the

search for new and suitable building blocks has always been an interesting task for synthetic chemists.⁸

3,4-ethylenedioxythiophene (**EDOT**), which can be easily polymerized into electroactive polymer films adhering on an electrode surface through electrochemical polymerization or copolymerization reactions, has been widely considered to be an ideal building block for **ECPs**.^{4,18} Its homopolymer, poly(3,4-ethylenedioxythiophene) (**PEDOT**) is a famous commercially-available **ECP** featuring cathodically coloring from light blue to deep blue with excellent electrochemical stability and low energy gap.^{5,19} To enhance the response speed and optical contrast of **PEDOT**, many attempts have been made such as adjusting its conjugated structure through copolymerization and modifying its morphology via a nanoporous structure.²⁰⁻²² However, there has been no detailed report on improving the interface contacting behavior between the electrolyte and **ECP** films.

Introduction of appropriate fluorine containing building blocks has been reported to alter the wettability and conjugation of the resultant polymer and would have positive effect on the electrochromic performances of the obtained **ECPs**. Cho et al. synthesized perfluoro-substituted **PEDOT** with enhanced resistance to the moisture.²³ Xu et al. incorporated F atoms onto benzothiadiazole acceptor and prepared an **ECP** with lower energy band gap and improved n-doping performance.²⁴ Inspired by their work, we designed and synthesized a new fluorine-containing monomer 3-(N-trifluoroacetamido)thiophene (**F-TH**, Scheme 1), its molecular structure in the solid state was also determined for the first time. Novel fluorinated conjugated copolymer **P(F-TH:EDOT)** was prepared subsequently via electrochemical copolymerization of **F-TH** and **EDOT**. Compared with the parent **PEDOT** film, the sponge-like nanoporous **P(F-TH:EDOT)** film not only exhibits reduced hydrophilicity and increased oleophilicity, but also presents excellent electrochromic performances with higher optical contrast, shorter coloring time and better coloration efficiency.

Scheme 1. Synthesis route of **F-TH** monomer.

The molecular structure of **F-TH** in solid state was determined via sXRD analysis. Colorless single crystals of **F-TH** suitable for sXRD analysis were grown via recrystallization and processed in CH₂Cl₂/CH₃CN (1:1, by volume) solution at room temperature. **F-TH** crystallizes in the orthorhombic non-centrally symmetric *Pca*2₁ space group with three similar molecules in one asymmetric unit,

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orientational disorder of the thienyl rings and F atoms are observed. A summary of the crystal data, collection parameters and refinement is given in Table S1, selected bond lengths (Å) and angles (°) are shown in Table S2.

Figure 1. Molecular structure of **F-TH** with partial atom numbering scheme, H-atoms have been omitted for clarity (red = O, blue = N, gray = C, green = F, yellow = S), only one of the three independent molecules in the unit cell is shown.

As depicted in Fig. 1, the structure of a **F-TH** molecule contains one S atom belonging to 3-thienyl ring, one N atom and one O atom belonging to an amide group, and three F atoms belonging to a CF₃ group. All the C—F bond lengths (1.29~1.36 Å) approach the standard value for a C(sp²)—F single bond, and the C—O bonds (1.21~1.24 Å) display double bond character, while the two type of C—N bond lengths are significantly different (Table S2), the C3_1—N1_1 (1.429(10) Å) bond exhibits single bond character but the C5_1—N1_1 (1.297(12) Å) bond length do not differ significantly from the C(sp²)=N(sp²) standard value of 1.29 Å,²⁵ indicating the partial double-bond feature of the amide bonds. As shown in Fig. 2, there are amide-amide intermolecular hydrogen bonds connecting adjacent molecules to form one-dimensional chains lying parallel to the c axis (Table S3), which further extend into a 3D supramolecular structure through Van der Waals interactions.

Figure 2. Molecular packing of **F-TH**, with H atoms omitted for clarity.

The distributions of the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) computed at the B3LYP/6-311+G (d, p) level for the molecules of **F-TH**, thiophene and **EDOT** are illustrated in Fig. 3. Calculation results indicate that the **F-TH** molecule has 49 occupied MOs, much more complicated in comparison with that of thiophene (22 occupied MOs) and **EDOT** (37 occupied MOs). The DFT calculations results of the HOMO level, LUMO level and HOMO-LUMO energy gap (E_g) of **F-TH** and **EDOT** are presented in Table S4. In these molecules, both the HOMOs and LUMOs are mostly π -antibonding type orbitals, **F-TH** has lower HOMO and LUMO levels than that of thiophene and **EDOT**. HOMO-LUMO energy separation has been used as a simple indicator of kinetic stability,^{26,27} the calculated E_g of **F-TH** is 5.98 eV, which is a bit smaller

than E_g of thiophene (5.99 eV), and is larger than E_g of **EDOT** (5.61 eV) owing to strong electron-withdrawing ability of CF₃ group. These calculation results imply that **F-TH** may exhibit lower kinetic stability and higher chemical reactivity compare with **EDOT**.

Figure 3. Molecular orbital surfaces and energies for the HOMO and LUMO of **EDOT**, **F-TH** and thiophene.

Due to the molecular structure of **F-TH**, we found it is very difficult to obtain good homopolymer film from **F-TH** through electrochemical polymerization, which prompted us to consider about the copolymerization of **F-TH** with **EDOT**. In another aspect, the presence of **F-TH** units will affect the electro-optical properties of obtained film. In an initial study, copolymer **P(F-TH:EDOT)** films were prepared by electrochemical polymerization using a 1:1 molar ratio of **F-TH** with **EDOT** on indium-tin-oxide (ITO) coated glass substrates by a potentiostatic method at 1.4 V (Scheme 2).

Scheme 2. Electrochemical polymerization of copolymer **P(F-TH:EDOT)**.

As shown in Fig. 4, both **P(F-TH:EDOT)** and **PEDOT** films' surface have a fibril morphology, but the fibers in **P(F-TH:EDOT)** are generally thinner than those in **PEDOT**. Besides, fibers in **PEDOT** are partly agglomerated together and form a rough surface with disordered pores (Fig.4a, Fig.4b), in **P(F-TH:EDOT)**, the reticular fibers formed a loose sponge-like nanoporous network, which is more favorable for ions insertion and extraction (Fig.4c, Fig. 4d).

Figure 4. SEM images of **PEDOT** taken at a magnification of (a) 25k and (b) 100k; SEM images of **PEDOT P(F-TH:EDOT)** taken at a magnification of (c) 25k and (d) 100k.

In order to evaluate their properties, the **P(F-TH:EDOT)** and **PEDOT** films were electrodeposited onto indium-tin-oxide (ITO) coated glass having dimensions of 2.6 cm × 0.9cm at a constant potential of 1.4 V versus Ag/AgCl and passing charge of 0.05 C to form films with an average thickness of ~86.9 nm for **P(F-TH:EDOT)** and ~85.3 nm for **PEDOT**. As shown in Fig. 5, water and acetonitrile droplet contact angle measurements performed on **P(F-TH:EDOT)** and **PEDOT** films revealed significant differences in the wettability. **P(F-TH:EDOT)** exhibits a contact angle with water of 56.9° (Fig. 5a) larger than that of **PEDOT** (33.5°, Fig. 5b), indicating that **P(F-TH:EDOT)** has a reduced hydrophilic surface compared to **PEDOT**. According to previous reports, most **EDOT**-containing polymers are sensitive to moisture in their neutral state,²⁸ **P(F-TH:EDOT)** with reduced hydrophilicity is expected to increase its resistance to environmental moisture.²³ On the other hand, **P(F-TH:EDOT)** exhibits a contact angle with acetonitrile of 10.9° (Fig. 5c), smaller than that of **PEDOT** (25.3°, Fig. 5d), indicating that **P(F-TH:EDOT)** has a better oleophilic wetting behavior than **PEDOT**. Wettability has an important impact on electrode materials' electrochemical performance. Although few studies mentioned the relationship of electrochromic properties with contacting behavior of electrode-electrolyte interfaces in **ECPs**, it has been widely studied in batteries and supercapacitors that wettability of electrodes to electrolyte is strongly related with the capacity and high-rate dischargeability. To date, lots of researches have been focused on improving the electrode-electrolyte wettability to enhance the utilization of electrode capacity and decrease electrolyte resistance.²⁹⁻³³ It can be inferred that the enhanced wettability of **P(F-TH:EDOT)** to acetonitrile probably will be beneficial to improve the electrochromic performances of **P(F-TH:EDOT)** in the electrolyte of acetonitrile.

Figure 5. Water droplet contact angles of (a) **PEDOT** and (b) **P(F-TH:EDOT)**, CH_3CN droplet contact angle of (c) **PEDOT** and (d) **P(F-TH:EDOT)**.

P(F-TH:EDOT) and **PEDOT** exhibit similar electrochemical behavior in 0.1 mol·L⁻¹ LiClO₄/CH₃CN solution. As shown in Fig. 6a, cyclic voltammetry (CV) curve of **P(F-TH:EDOT)** displays two significant oxidation peaks ($E_{p,a} = 0.30$ V and $E_{p,a'} = 1.10$ V) and an obvious reduction peak ($E_{p,c} = -0.74$ V). The reduction peak (c) and first oxidation peak (a) are attribute to the redox steps on conversion from the neutral (insulating) state to conducting (oxidized) state,^{50,5p} while the second oxidation peak (a') is probably contribute to the over-oxidation which will accelerate polymer degradation.^{5j} CV curve of **PEDOT** displaying also two oxidation peaks ($E_{p,a} = 0.30$ V and $E_{p,a'} = 1.21$ V) and a reduction peak ($E_{p,c} = -0.69$ V). The first oxidation peak of **P(F-TH:EDOT)** and **PEDOT** appears at the same potential, but both the second oxidation peak and the reduction peak of **P(F-TH:EDOT)** were shifted to a lower potential ($E_{p,a'} = 1.21 \rightarrow 1.10$ V, $E_{p,c} = -0.69 \text{ V} \rightarrow -0.74$ V) compared to that of **PEDOT**. Besides, **P(F-TH:EDOT)** exhibited substantially larger current density than **PEDOT**, proving that **P(F-TH:EDOT)** has higher electrochemical activity in comparison with **PEDOT**. As shown in Fig. S12, **P(F-TH:EDOT)** film is stable and preserves its electroactivity at high scan rates. The peak current densities $j_{p,a}$, $j_{p,a'}$ and $j_{p,c}$, were all proportional to the scan rate, which indicated that the electrochemical processes are non-diffusion controlled.³⁴

Figure 6. CV curves of the **P(F-TH:EDOT)** (red) and **PEDOT** (black) in 0.1 mol·L⁻¹ LiClO₄/CH₃CN solution at a sweep rate of 50 mV·s⁻¹.

Nyquist representation of the impedance spectra of **P(F-TH:EDOT)** and **PEDOT** films modified electrodes were collected in the frequency range of 10^5 - 1 Hz in $0.1 \text{ mol}\cdot\text{L}^{-1}$ $\text{LiClO}_4/\text{CH}_3\text{CN}$ solution (Fig. 7). In the high frequency range, the spectra include semicircles which are attributed to the processes at the ITO/film and film/solution interfaces, while the low frequency part corresponds to the charge transport processes in the bulk of the film. The impedance spectra could be fitted using the equivalent circuit shown in Fig. 7b. The circuit can be decomposed in three elements connected in series: (i) the cell resistance R_s , (ii) the impedance at the electrode/solution interface modelled by a parallel combination of the charge transfer resistance R and a capacitance C_i , (iii) the impedance associated to the charge transport in the bulk of the film composed of a parallel combination of a constant phase element CPE_F and a Warburg element W_F (Table S6). The charge transfer resistance of **P(F-TH:EDOT)** is 20.6Ω lower than that of **PEDOT** (28.9Ω), which confirms that **P(F-TH:EDOT)** film is more efficient and faster to exchange ions with the solution. In addition, W_F value for **P(F-TH:EDOT)** is higher than that of **PEDOT**, which can be attributed to the faster ion diffusion coefficient in **P(F-TH:EDOT)** film. These results are probably due to the enhanced wettability to electrolyte solution and the sponge-like nanoporous network of **P(F-TH:EDOT)** which supplies sufficient ion-transfer highways to promote the electrolyte penetration.

Figure 7. (a) Nyquist plots of the impedance spectra of **P(F-TH:EDOT)** (red) and **PEDOT** (black) modified electrodes measured in $0.1 \text{ mol}\cdot\text{L}^{-1}$ $\text{LiClO}_4/\text{CH}_3\text{CN}$, (b) Equivalent circuit used to fit the spectra.

Visible and NIR transmission spectra of **P(F-TH:EDOT)** and **PEDOT** films at different potentials (-0.8 to 0.8 V) are shown in Fig. 8. As determined by the onset of the π - π^* transition,³⁵ the **P(F-TH:EDOT)** films obtained under these conditions has a band gap of ca. 1.61 eV (771 nm), slightly larger than that of **PEDOT** films (1.53 eV , 809 nm). Similar to **PEDOT**, **P(F-TH:EDOT)** is a cathodically-colored film with a color change from deep blue at -0.8 V to transmissive sky-blue in the oxidized state at 0.8 V . In the neutral state, the visible absorption band of **P(F-TH:EDOT)** centered at 616 nm is attributed to the π - π^* transition,³⁶ which is a bit blue-shifted compared with that of **PEDOT** (620 nm). As the potential increases to the oxidized state, the visible absorption of **P(F-TH:EDOT)** gradually decreases, but a new NIR absorption related to the electronic transition of the polaron and the dipolaron of the doped ions strengthens.³⁷

Figure 8. Spectroelectrochemical spectra of (a) **PEDOT** and (b) **P(F-TH:EDOT)** with different applied potentials between -0.8 V and 0.8 V .

Coloration efficiency (CE) is one of the most important characteristics for **ECPs**. Calculating on the basis of Fig. 9a and Fig. 9b, the CE value of **P(F-TH:EDOT)** achieves up to $167.9 \text{ cm}^2\text{C}^{-1}$, 55% higher than that of **PEDOT** ($108.1 \text{ cm}^2\text{C}^{-1}$, ESI). As shown in Fig. 9c and Fig. 9d, **P(F-TH:EDOT)** exhibits improved electrochromic properties with higher optical contrast (55% at 616 nm) and shorter coloring time (0.70 s) compared to **PEDOT** (43% optical contrast at 620 nm , 1.57 s coloring time). In comparison with previous reported **PEDOT** and its analogs,⁵ **P(F-TH:EDOT)** also exhibits relative short coloring time and bleaching time (Table S7). These phenomena may be also attributed to the enhanced wettability to electrolyte solution of **P(F-TH:EDOT)**.

Figure 9. The simultaneous monitoring of (a) transmittance and (b) switching current for **P(F-TH:EDOT)** film (green) monitored at 616 nm and **PEDOT** film (blue) monitored at 620 nm , switching response for (c) **P(F-TH:EDOT)** and (d) **PEDOT** films monitored at corresponding wavelengths in $0.1 \text{ mol}\cdot\text{L}^{-1}$ $\text{LiClO}_4/\text{CH}_3\text{CN}$ solution between their neutral (-0.8 V) and oxidized (0.8 V) states at 5 s intervals.

As shown in Fig. S13, **P(F-TH:EDOT)** exhibits a contact angle with propylene carbonate (PC) of 13.04° smaller than that of **PEDOT** (37.82°), indicating that **P(F-TH:EDOT)** also has better wettability to propylene carbonate compared with **PEDOT**. Electrochemical studies confirm that the **P(F-TH:EDOT)** film is more efficient than **PEDOT** to exchange ions with the solution of $0.1 \text{ mol}\cdot\text{L}^{-1}$ LiClO_4/PC (Fig. S14, ESI). As shown in Fig. S15, **P(F-TH:EDOT)** presents enhanced electrochromic properties with higher optical contrast (58% at 619 nm) and shorter coloring time (3.41 s) and higher CE value ($191.2 \text{ cm}^2\text{C}^{-1}$) compared to **PEDOT** (54% optical contrast at 622 nm , 3.91 s coloring time, $153.8 \text{ cm}^2\text{C}^{-1}$ CE value) in $0.1 \text{ mol}\cdot\text{L}^{-1}$ LiClO_4/PC .

In summary, the new fluorine-containing monomer **F-TH** was synthesized and characterized for the first time. Its molecular structure was determined by a single-crystal X-ray study. **F-TH** functions as a building block in electropolymerization with **EDOT** gives a novel copolymer **P(F-TH:EDOT)** subsequently. Compared with the parent homopolymer **PEDOT** film, sponge-like nanoporous **P(F-TH:EDOT)** film has a slightly larger band gap with a reduced hydrophilic and increased oleophilic surface. Spectroelectrochemical analysis results reveal that **P(F-TH:EDOT)** exhibits excellent electrochromic performances with higher optical contrast (55%) and much shorter coloring time (0.70 s) than that of **PEDOT** (43%, 1.54 s). The coloration efficiency value of **P(F-TH:EDOT)** achieves up to 167.9 cm²/C, 55% higher than that of **PEDOT** (108.1 cm²/C). These improved electrochromic properties of **P(F-TH:EDOT)** are probably related with the enhanced wettability to electrolyte. This work not only provides a new approach for the preparation of **ECP** film with suitable properties, but also provides an important direction to improve electrochromic performances of **ECP** film through adjusting their electrode-electrolyte interface contacting behavior.

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Conflicts of Interest

There are no conflicts to declare.

Keywords: wettability • electropolymerization • molecular structure • electrochromic conjugated polymers • impedance spectra

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