Blue to Light Gray Electrochromic Polymers from Dodecyl-Derivatized Thiophene *Bis-*Substituted Dibenzothiophene/Dibenzofuran

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ABSTRACT: 3-Dodecylthiophene end-capped two monomers: 2,8-*bis*-(4-dodecyl-thiophen-2-yl)-dibenzothiophene (DBT-3DTh) and 2,8-*bis*-(4-dodecyl-thiophen-2-yl)-dibenzofuran (DBF-3DTh) were synthesized via Stille coupling reaction. Both monomers exhibited emission peaks at about 400 nm with fluorescence quantum yields ranging from 0.16 to 0.21. The corresponding electroactive polymers poly(2,8-*bis*-(4-dodecyl-thiophen-2-yl)-dibenzothiophene) (PDBT-3DTh) and poly(2,8-*bis*-(4-dodecyl-thiophen-2-yl)-dibenzothiophene) (PDBT-3DTh) and poly(2,8-*bis*-(4-dodecyl-thiophen-2-yl)-dibenzotion method and displayed good electro-chemical stability. Both polymers switched between light gray in the neutral state and blue in the oxidized state. Kinetic inves-

tigations showed that PDBT-3DTh exhibited a maximum optical contrast (ΔT %) of 25.23% at 575 nm with the coloration efficiency (CE) of 196 cm² C⁻¹. However, the electrochromic properties of PDBF-3DTh were inferior to PDBT-3DTh. Further detailed discussions with EDOT and 3-alkylthiophenes end-capped DBT/DBF hybrid electrochromic polymers were comparatively studied. © 2015 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2016**, *54*, 1468–1478

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INTRODUCTION Electrochromism is commonly defined as the visible and reversible change in the transmittance of a material caused by a definite applied voltage.¹ Conjugated polymers as electrochromic materials have been extensively investigated since they show excellent electrochemical and optical properties including processability, fast switching time, high optical contrast, and ability to modify their structure to achieve multicolored polymers.² Therefore, extensive investigations on the design and synthesis of electrochromic polymers using of new, different inner and end units with excellent electrochemical and electrochromic performance have been the major attractive area. In recent years, fluorenes/carbazoles as inner units to synthesize novel electrochromic polymers have exhibited many excellent advantages such as excellent chemical stability, ease of synthesis and modification, good electrical conductivity, and plentiful color changes switching between the reduced and oxidized ${\rm states.}^{3-5}$ However, excimer formation in the solid state, and high-energy barrier for hole injection limit their application.⁶ To circumvent these obstacles, a promising way to improve charge injection and optical properties is replacing the inner units with their close analogs dibenzothiophene (DBT) and dibenzofuran (DBF).

As high triplet energy host materials of blue PHOLEDs, DBT, and DBF,^{7,8} with a planar π -conjugated structure, have been typically used to improve the quantum efficiency in PHO-LEDs. Moreover, Zhou et al. have studied PDBF electropolymerized in boron trifluoride diethyl etherate which revealed good redox activity and excellent fluorescence properties, as demonstrated from our previous reports.9 PDBT, as new materials applied in electrochromic devices, shows good hole-transporting ability, emission properties, and rigid planarity, which makes it a good candidate for constructing host materials.¹⁰ Given that, a series of EDOT and 3alkylthiophenes end-capped DBT/DBF hybrid electrochromic polymers (Scheme 1; PDBT-EDOT, PDBF-EDOT, PDBT-Th, PDBF-Th, PDBT-3MeTh, PDBF-3MeTh, PDBT-3HexTh, PDBF-3HexTh) have been researched deeply in our lab on their electrochemical and electrochromic performance.^{11,12} However, their solubility cannot meet the demands in real life. Moreover, because of their outstanding electro-optical properties of 3-alkylthiophenes end-capped DBT/DBF hybrid electrochromic polymers, it is necessary to detect the rule of performance with the increase in the length of alkyl chain attached to the thiophene units. Meanwhile, 3dodecylthiophene, as one kind of 3-alkylthiophene, whose

Kaiwen Lin and Yao Zhao contributed equally to this work. Additional Supporting Information may be found in the online version of this article. © 2015 Wiley Periodicals, Inc.



SCHEME 1 Designed and previously synthesized DBT/DBF-heterocycle hybrid electrochromic polymers in our lab. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

flexible alkyl side chains attached to the stiff backbones endow them high solubility in common organic solvents, and it has been utilized as the end unit in many systems⁵.

Keeping all these in mind and combine the both merits of inner units DBT/DBF and end unit 3-dodecylthiophene, DBT-3DTh and DBF-3DTh were herein synthesized via Stille coupling reaction. Both two neutral state light gray electrochromic polymers (PDBT-3DTh and PDBF-3DTh, Scheme 2) based on DBT-3DTh and DBF-3DTh were electropolymerized. Furthermore, their electrochemical and thermal properties, spectroelectrochemical properties, and electrochromic properties were investigated in detail. Further discussions with EDOT and 3-alkylthiophenes end-capped DBT/DBF hybrid electrochromic polymers were comparatively studied.

EXPERIMENTAL

Chemicals

3-Dodecylthiophene (98%; J&K Scientific Ltd), bromine, glacial acetic acid, methanol, *n*-butyllithium (2.5 mol L⁻¹ in hexane; Energy Chemical) and chlorotributyltin (98%; Energy Chemical) were all used as received without further treatment. Dibenzothiophene (DBT, 99%; Energy Chemical), dibenzofuran (DBF, 99%; Energy Chemical) and tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄, 99%; Energy Chemical) were stored at 4 °C and used as received. Tetrabutylammonium hexafluorophosphate (Bu₄NPF₆, 98%; Energy Chemical) was dried under vacuum at 60 °C for 24 h before use. Tetrahydrofuran (THF), dichloromethane (DCM), and acetonitrile (MeCN) were all analytical grade and purchased from Beijing East Longshun Chemical Plant and used after reflux distillation.

Instrumentation

NMR spectra were recorded on a Bruker AV 400 NMR spectrometer with $CDCl_3$ or $DMSO-d_6$ as the solvent and tetramethylsilane as an internal standard (TMS, singlet, chemical shift: 0.0 ppm). UV-Vis spectra of the monomers dissolved in MeCN were taken by using Perkin-Elmer Lambda 900 Ultraviolet-Visible Near-Infrared spectrophotometer. With an F-4500 fluorescence spectrophotometer (Hitachi), the fluorescence spectra of the monomers and polymers were determined. Infrared spectra were determined with a Bruker Vertex 70 Fourier-transform infrared (FT-IR) spectrometer with samples in KBr pellets. Thermogravimetric analysis (TGA) was performed with a Pyris Diamond TG/DTA thermal analyzer (PerkinElmer) under a nitrogen stream from 290 to 1100 K at a heating rate of 10 K min⁻¹. Scanning electron microscopy (SEM) measurements were made by using a VEGA II-LSU scanning electron microscope (Tescan) with the polymer films deposited on the ITO-coated glass.

Synthesis of Monomers 2,8-Dibromodibenzothiophene

Bromine (3.1 mL, 60.5 mmol) was added dropwise to a mixture of DBT (5.0 g, 27.1 mmol) and chloroform (30 mL) at 0 °C.¹³ Under nitrogen atmosphere the reaction mixture was vigorous stirred 12 h at room temperature. The crude product was filtered off and washed with methanol to isolate 2,8dibromodibenzothiophene. The product was obtained as a white powder in 85% yield.

¹H NMR (400 MHz, CDCl₃, ppm): 7.38 (d, J = 1.6 Hz, H), 7.41 (d, J = 2 Hz, H), 7.52 (s, H), 7.54 (s, H), 8.05 (d, J = 2 Hz, 2H); ¹³C NMR (400 MHz, CDCl₃, ppm): 138.74, 136.43, 130.71, 125.78, 125.48, 118.72.



SCHEME 2 Synthetic routes of monomers and corresponding polymers. Reagents and conditions: (i) X = S; CHCl₃, Br₂ (2.2 eq), N₂; (ii) X = O; CH3COOH, Br₂ (2.2 eq), N₂; (iii) Pd(PPh₃)₄, THF, 90 °C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

2,8-Dibromodibenzofuran

A 250 mL round bottom flask containing 8.4 g (50 mmol) dibenzofuran dissolved in 100 mL glacial acetic acid equipped with an addition funnel.¹⁴ Bromine 5.1 mL (100 mmol) in 30 mL glacial acetic acid was added dropwise via the addition funnel to dibenzofuran under vigorous stirring. This reaction mixture was stirred at room temperature for 4 h. After refluxed for 6 h, the reaction was cooled to room temperature. The solid was collected by filtration and washed for three times with 100 mL portions of water. Recrystallized from 100 mL acetic anhydride and obtained 12.2 g pure white solid 2,8-dibromodibenzofuran in 75% yield.

¹H NMR (400 MHz, CDCl₃, ppm): δ 7.44 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 8.03 (d, *J* = 4.0 Hz, 2H).

Synthesis of the Stannylation of 3-Dodecylthiophene

A solution of 3-dodecylthiophene (2.52 g) in dry THF (30 mL) was cooled to -78 °C and blanked by nitrogen for three times.¹⁵ *n*-BuLi (2.5 mol L⁻¹ in hexane, 4.8 mL) was added dropwise to the solution within 30 min. The mixture was stirred for 1.5 h at -78 °C and then warmed to -40 °C. Chlorotributyltin (1.73 g) was added slowly to the solution, and after that, the temperature was slowly warmed to room temperature. And the mixture was stirred at room temperature for 12 h under argon atmosphere. The residue was filtered and the solvent removed under reduced pressure by rotary evaporation. The tributylstannane compound was used directly for the Stille coupling reaction without further purification.

2,8-Bis-(4-Dodecyl-Thiophen-2-yl)-Dibenzothiophene (DBT-3DTh)

DBT-3DTh was synthesized via Stille coupling reaction as described in Scheme 2. To a mixture solution of 2,8-dibromodibenzothiophene (1.0 g, 2.9 mmol) and tributyl(3-dodecylthiophene-2-yl) stannane (7.8 g, 14.5 mmol) in dry THF (50 mL), Pd(PPh₃)₄ (0.165 g) was added as the catalyst. The mixture was stirred magnetically at room temperature under nitrogen atmosphere. After half an hour, the mixture was heated to reflux with vigorous stirring for another 24 h, and then concentrated under reduced pressure. Finally, column chromatography was used to purify the reaction mixture. The product was obtained as a white powder in 65% yield.

¹H NMR (400 MHz, CDCl₃, ppm): δ 8.38 (s, 2H), 7.83 (d, J = 7.4 Hz, 2H), 7.72 (dd, J = 12.2 Hz, 2H), 7.28 (d, J = 12.4 Hz, 2H), 6.94 (s, 2H), 2.66 (t, J = 15.8 Hz, 4H), 1.71 (m, 4H), 1.31 (m, 36H), 0.92 (m, 6H). ¹³C NMR (400 MHz, CDCl₃, ppm): 143.97, 143.34, 138.36, 135.40, 131.07, 124.63, 124.28, 122.61, 118.98, 118.08, 31.40, 30.21, 30.00, 29.16, 29.13, 28.99, 28.88, 28.83, 22.16, 17.01, 13.56, 13.04.

2,8-Bis-(4-Dodecyl-Thiophen-2-Yl)-Dibenzofuran (DBF-3DTh)

The synthetic method of DBF-3DTh is similar to DBT-3DTh, which was synthesized via Stille coupling reaction as

¹H NMR (400 MHz, $CDCl_3$, ppm): δ 8.19 (s, 2H), 7.72 (t, J = 11.8 Hz, 2H), 7.55 (d, J = 8.2 Hz, 2H), 7.24 (s, 2H), 6.91 (s, 2H), 2.66 (t, J = 15.8 Hz, 4H), 1.70 (m, 4H), 1.31 (m, 36H), 0.92 (m, 6H). ¹³C NMR (400 MHz, $CDCl_3$, ppm): 156.15, 144.43, 143.93, 130.12, 125.69, 124.65, 124.53, 119.27, 117.87, 111.99, 31.93, 30.72, 30.50, 29.69, 29.63, 29.51, 29.39, 29.36, 22.69, 17.53, 14.11, 13.59.

Electrochemistry

All the electrochemical experiments and polymerization of monomers were performed in a one-compartment cell with the use of Model 263A potentiostat-galvanostat (EG&G Princeton Applied Research) under computer control. For electrochemical tests, the working and counter electrodes were both Pt wires with a diameter of 1 mm, while the reference electrode (RE) was Ag/AgCl. The Ag/AgCl RE was prepared electrochemically by chronoamperometry method at potential of 1.5 V for 100 s in hydrochloric acid (6 mol L^{-1}) and calibrated against the SCE system. Bu₄NPF₆ $(0.1 \text{ mol } \text{L}^{-1})$ was used as electrolyte, dissolved in DCM/ MeCN (50/50, v/v) which was freshly distilled before its use. All the solutions were deaerated by a dry nitrogen stream and maintained under a slight overpressure through all the experiments. Polymer films were obtained electrochemically in potentiodynamic regime. After polymerization, the films were washed repeatedly with anhydrous MeCN to remove the electrolyte and monomer.

The cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were employed to evaluate the HOMO, LUMO levels and E_g values of monomers according to the empirical equations as follow:¹⁶

$$HOMO = -(E_{ox} + 4.80) eV$$
 (1)

$$LUMO = (HOMO + E_{g,opt}) eV$$
 (2)

where E_{ox} and $E_{g,\text{opt}}$ are the onset oxidation potential and the optical bandgap of compounds, respectively.

Electrochromic Experiments

Spectroelectrochemistry and kinetic studies were recorded on a Specord 200 plus (Analytik Jena) spectrophotometer and the potentials were cont rolled using Versa STAT 3 (Princeton Applied Research). The spectroelectrochemical cell consisted of a quartz cell, an Ag/AgCl electrode as reference electrode, a Pt wire as counter electrode, and an indium tin oxide (ITO) coated glass as the transparent working electrode. All measurements were carried out in MeCN containing Bu_4NPF_6 (0.1 mol L⁻¹).

The optical density (Δ OD) at the specific wavelength (λ) was determined by Δ *T*% values of electrochemically oxidized and reduced polymer films, using the following equation:¹⁷

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TABLE 1 The Onset Oxidation Potentials of DBT/DBF-Heterocycle Hybrid Monomers

Samples	DBT-EDOT	DBF-EDOT	DBT-Th	DBF-Th	DBT-3MeTh	DBF-3MeTh	DBT-3HexTh	DBF-3HexTh	DBT-3DTh	DBF-3DTh
E _{ox,onset} (V)	0.91	0.95	1.12	1.21	1.11	1.23	1.03	1.11	1.05	1.12

$$\Delta OD = \log(T_{\rm ox}/T_{\rm red}) \tag{3}$$

The coloration efficiency (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 (Δ OD) at the specific wavelength (λ) of the sample as illustrated by the following equation:¹⁸

$$CE = \Delta OD/Q_d \tag{4}$$

RESULTS AND DISCUSSION

Monomer Synthesis

The synthetic routes of DBT-3DTh and DBF-3DTh are revealed in Scheme 2. These two monomers were synthesized via Stille cross coupling reaction. Importantly, these two monomers were synthesized and their properties were investigated for the first time as far as we know. NMR and FT-IR spectra of some intermediates and target compounds are displayed in Supporting Information Figures S1 to S6 and Table S1, respectively.

Electrochemical Polymerization of DBT-3DTh and DBF-3DTh

Supporting Information Figure S7 shows anodic polarization curves of 0.01 mol L⁻¹ monomers in DCM/MeCN-Bu₄NPF₆ $(0.1 \text{ mol } L^{-1})$. The monomers can easily dissolve in DCM, and partially dissolve in MeCN (formed flocculus). And the electrochemical polymers became rough, discontinuous, and heterogeneous when electropolymerized in DCM-Bu₄NPF₆ or in MeCN-Bu₄NPF₆ rather than their mixture. Therefore, a mixture of DCM and MeCN (50/50, v/v) was chosen as the solvent system to obtain the polymer films on an ITO coated glass slide. The onset oxidation potential $(E_{\text{ox.onset}})$ of DBT-3DTh was 1.05 V versus Ag/AgCl, lower than DBF-3DTh (1.12 V vs. Ag/AgCl), which was caused by smaller overlap integral of oxygen atom compared with sulfur atom in the dibenzo-five-membered ring. Deeply, to find the relationship between their structures and properties, all the $E_{\rm ox,onset}$ values of DBT/DBF-heterocycle hybrid monomers^{11,12} were offered in Table 1, and all values were detected in the same experimental conditions. Among them, EDOT end-capped monomers, DBT-EDOT and DBF-EDOT, were 0.91 V and 0.95 V versus Ag/AgCl, lower than those of thiophene and alkylthiophene end-capped monomers. This is an expected result since EDOT as the strong electron-donating group increases the electron density of DBT/DBF system and makes their oxidation relatively easy. Further, the $E_{\text{ox.onset}}$ values of 3-DTh and 3-HexTh end-capped monomers were less than Th and 3-MeTh end-capped monomers, which can be ascribed to the electron-donating ability of the alkyl chain. Meanwhile, the dodecyl chain was electron richer relative to the hexyl group, but 3-DTh end-capped monomers exhibited relatively

high oxidation onset potentials than 3-HexTh end-capped monomers. The phenomenon was mainly attributable to significant steric hindrance in the large alkyl chain. In addition, DBF-based monomers were higher than DBT-based monomers when the end units were the same. Lower electronegativity, larger atomic size, and better polarizability of sulfur atom than oxygen atom resulted in DBT-based systems electron richer than DBF-based systems.

Figure 1 shows cyclic voltammograms (CVs) corresponding to the potentiodynamic electropolymerization of two monomers. During repetitive cycling of electrolytes containing the corresponding monomers, new reversible redox couples emerged at 0.8 to 1.0 V versus Ag/AgCl. As the cyclic scan continued, the increase of anodic and cathodic peak current densities in CVs implied that the amount of the polymer films increased on the surface of working electrode. In particular, electrochemical polymerization of DBT-3DTh revealed



FIGURE 1 Cyclic voltammograms of 0.01 mol L^{-1} DBT-3DTh (A) and DBF-3DTh (B) in DCM/MeCN-Bu₄NPF₆ (0.1 mol L^{-1}). Potential scan rate: 100 mV s⁻¹.

TABLE 2 The Calculated and Experime	ental Parameters of DBT-3DTH and DBF-3DTH
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Compounds	HOMO (eV)	LUMO (eV)	$E_{\rm ox,onset}$ (V)	$E_{\rm g,opt}$ (eV)	$\lambda_{abs,max}$ (nm)	λ _{em,max} (nm)
DBT-3DTh	-5.85	-2.35	1.05	3.50	311	399
DBF-3DTh	-5.90	-2.37	1.10	3.53	308	400

an obvious redox couples without potential shift. To compare the redox peak potentials with structural analog, DBT-EDOT and DBF-EDOT exhibited obvious redox peaks at 0.55 to 0.80 V versus Ag/AgCl,¹¹ lower than those of thiophene and alkylthiophene end-capped polymers owing to the presence of the strong electron-donating group of EDOT. Thiophene end-capped polymers, DBT-Th and DBF-Th, displayed reversible peaks with oxidation potentials of 1.35 V and reduction potentials of about 1.10 V versus Ag/AgCl,¹² both values were higher than those of polymers with alkylthiophene as end units and DBT/DBF as inner units. The steric hindrance and electron-donating effect of alkyl chain may both play role on this process. Moreover, there are differences in the oxidation peak current density (from low to high), DBT-3MeTh (3.1 mA cm⁻², the 10th cycle, the same below) < DBT-3DTh (4.6 mA cm⁻²) < DBT-Th (5.2 mA cm⁻²) <DBT-3HexTh (9.7 mA cm⁻²); DBF-3MeTh (1.2 mA cm⁻²) < DBF-3DTh (1.8 mA cm⁻²) < DBF-3MeTh (2.3 mA cm⁻²) < DBF-Th (5.1 mA cm⁻²). The phenomenon could be ascribed to the interdigitation of alkyl chains attached on the thiophene ring, which is beneficial to the formation of high quality films.

The HOMO energy levels of monomers were calculated from linear sweep voltammetry from the intersection between base line and tangent drawn to the increasing current line. HOMO levels were -5.85 eV for DBT-3DTh and -5.90 for DBF-3DTh, respectively. The LUMO levels, estimated from the HOMO and the onsets of the absorption peaks, were found to be -2.35, and -2.37 eV for DBT-3DTh and DBF-3DTh, respectively (Table 2).

Optimisation of Electrical Conditions and Preparation of the Hybrid Polymers

To optimize the applied potential for polymerization, a set of current transients during the electropolymerization at different applied potentials were recorded, as shown in Supporting Information Figure S8. According to the experiment, PDBT-3DTh and PDBF-3DTh films used for the characterisation mentioned below were all prepared by the chronoamperometry method at constant potentials of 1.25 V and 1.30 V (equal to that of PDBF-3HexTh) vs. Ag/AgCl, respectively. Also, visual inspection demonstrated that PDBT-3DTh and PDBF-3DTh films with smooth, homogeneous, and continuous surfaces were formed at the optimal oxidation potentials, as predicted from their *I-t* curves, and they showed good adherence against the electrode.

Structural Characterization

FT-IR spectra of DBT-3DTh, DBF-3DTh, doped PDBT-3DTh, and doped PDBF-3DTh were recorded, as shown in Figure 2.

Also, the details of the band assignments for monomers and polymers are given in Supporting Information Table S1.

FT-IR spectra of the doped polymers PDBT-3DTh and PDBF-3DTh showed the characteristic peaks of corresponding monomers, which confirmed that the structure of DBT-3DTh and DBF-3DTh was not destroyed during the electrochemical polymerization process. The obviously broadening of polymers, in comparison with those of monomers, were similar to those of other conjugated polymers reported previously.¹⁹ More specifically, the absorption peaks of polymers at around 839 cm⁻¹ and 837 cm⁻¹ are due to the C-H out of plane bending vibrations of 2,3,5-trisubstituted thiophene ring.²⁰ Compared with the spectra of monomers, the disappearance of peaks at 723 and 725 cm⁻¹ which attributed to C-H bending vibrations of 2,4-substituted thiophene ring,



FIGURE 2 FT-IR spectra of DBT-3DTh, DBF-3DTh, doped PDBT-3DTh, and doped PDBF-3DTh. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



FIGURE 3 UV-Vis spectra of two monomers in MeCN and corresponding doped polymers electrodeposited on ITO. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

implied that the electrochemical polymerization occurred at α positions of two thiophene rings (Scheme 2), in good agreement with previous reports.^{11,12} In addition, the bands due to C_{α} -H stretching at approximately 3106 cm⁻¹ and C_{β} -H stretching at 3027 cm⁻¹ in the monomer spectra are nearly absent or weak, also indicating the occurrence of electropolymerization at the thiophene rings. All these results confirmed the occurrence of electrochemical polymerization among the monomers to form conducting polymers.

UV-Vis and Fluorescence Spectra of Monomers and their Corresponding Polymers

The UV-Vis spectra of both monomers dissolved in CH_3CN and corresponding doped polymers electrodeposited on ITO were examined, as shown in Figure 3. Both monomers exhibited similar characteristic π - π * transition peaks in the region of 256 to 311 nm, which coincided with their structural analog.^{11,12} On the contrary, the spectrum of both polymers showed a much broader absorption, which revealed an red-shifted peaks at 353 nm for PDBT-3DTh, and at 329 nm for PDBF-3DTh. The red shifts for these two polymers were attributed to their high conjugation length. Generally, the lon-

ger wavelength is the absorption, the higher conjugation length is the polymer.²¹ Therefore, the spectral results confirmed the occurrence of electrochemical polymerization.

The fluorescence spectra of the monomers and dedoped polymers dissolved in MeCN are illustrated in Figure 4. The emission peak of DBT-3DTh emerged at 399 nm when excited at 310 nm whereas a maximum emission peak at 475 nm characterised the spectrum of doped PDBT-3DTh when excited at 420 nm. A dominant maximum emission at 400 nm of DBF-3DTh was observed when excited at 305 nm, while doped PDBF-3DTh exhibited a maximum emission peak at 452 nm under excitation at 400 nm. The relatively small red shift observed for the monomers suggests that there is little geometric change between the ground and excited states. $^{\rm 22}$ Meanwhile, obvious red shifts could be observed between the monomers and soluble polymers (76 nm between DBT-3DTh and PDBT-3DTh and 52 nm between DBF-3DTh and PDBF-3DTh), which is primarily attributed to the elongation of the their delocalised $\pi\text{-}\mathrm{electron}$ chain sequence, called Stokes $\mathrm{shift.}^{23}$ For all the 3-alkylthiophenes end-capped DBT/DBF hybrid electrochromic polymers, with the increase in the length of alkyl chain (Scheme 1, $R = CH_3$, C_6H_{13} , $C_{12}H_{25}$) attached to the thiophene unit at third position, the main chain emission



FIGURE 4 Emission spectra of monomers and corresponding polymers in MeCN. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



FIGURE 5 Cyclic voltammograms of PDBT-3DTh (A) and PDBF-3DTh (B) modified Pt electrodes in monomer-free DCM/MeCN-Bu₄NPF₆ (0.10 mol L⁻¹) at different potential scan rates. Right: plots of redox peak current densities versus potential scan rates for PDBT-3DTh (C) and PDBF-3DTh (D). j_p is the peak current density, and $j_{p,a}$ and $j_{p,c}$ denote the anodic and cathodic peak current densities, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

appears at short wavelength, which can be ascribed to the large interchain π - π stacking distance and weak intermolecular interaction of polymers that make the polymers main chains decreased orbital overlap and conjugation.

The fluorescence quantum yields of DBT-3DTh and DBF-3DTh were measured with anthrancene in MeCN (standard, ϕ ref = 0.27)²⁴ as a reference and were calculated according to the well-known method given in eq 3:

$$\varphi_{\text{overall}} = \frac{n^2 A_{\text{ref}} I}{n_{\text{ref}}^2 A I_{\text{ref}}} \times \varphi_{\text{ref}}$$
(3)

where *n*, *A*, and *I* denote the refractive index of the solvent, the absorbance at the excitation wave length, and the intensity of the emission spectrum, respectively. The subscript ref denotes the reference, and no subscript denotes the sample. The absorbance of the samples and the standard should be similar.²⁵ By calculation, the fluorescence quantum yields were 0.21 for DBT-3DTh and 0.16 for DBF-3DTh, respectively.

Electrochemistry of the Polymers

For the sake of getting a deeper insight into the electrochemical activity and stability of as-formed polymer films, the

electrochemical behaviors of PDBT-3DTh and PDBF-3DTh by cyclic voltammetry in monomer-free DCM/MeCN-Bu₄NPF₆ $(0.1 \text{ mol } L^{-1})$ were investigated, as shown in Figure 5. A redox process was observed between 0.75 V and 1.06 V for PDBT-3DTh; between 0.65 V and 1.30 V for PDBF-3DTh. PDBT-3DTh exhibited a lower oxidation potential (0.98 V) than PDBF-3DTh (1.15 V), which can be attributed to the presence of more polarizable sulfur atom. In particular, CVs of PDBF-3DTh showed an obvious hysteresis, i.e., an obvious potential shift of redox peaks. This phenomenon is hardly explained by conventional kinetic limitations such as ion diffusion or interfacial charge transfer processes.²⁶ The main reasons are usually slow heterogeneous electron transfer, local rearrangement effect of polymer chains, and electronic charging of interfacial exchange corresponding to the metal/ polymer and polymer/solution interfaces.²⁷ On the other hand, the peak current densities was proportional to potential scanning rates for both films, indicating that the redox process was nondiffusional and the electroactive polymers were well adhered to the working electrode surface.²⁸

As far as we can know from CVs of all the 3-alkylthiophenes end-capped DBT/DBF hybrid polymers, with the elongation



FIGURE 6 Long-term cyclic voltammograms of PDBT-3DTh (A) and PDBF-3DTh (B) in monomer-free DCM/MeCN-Bu₄NPF₆ (0.1 mol L⁻¹). Potential scan rate: 150 mV s⁻¹. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

of the alkyl chain length (Scheme 1, $R = CH_3$, C_6H_{13} , $C_{12}H_{25}$), the corresponding polymer exhibited sharper redox peaks in comparison with that of PDBT-Th and PDBF-Th, implying faster doping/dedoping processes of alkyl thiophene based polymers. This phenomenon probably results from the steric hindrance from the alkyl chains, which causes the polymer chains to separate from each other. The separation generally promotes a more expanded morphology and facilitates the transport of counter balancing ions across the conjugated block, and thus usually favors fast switching of conjugated polymers.⁵

The long-term stability of the redox activity for PDBT-3DTh and PDBF-3DTh was investigated in DCM/MeCN-Bu₄NPF₆ (0.1 mol L⁻¹) at the potential scan rate of 150 mV s⁻¹, as shown in Figure 6. The polymer films exhibited good stability, for the amount of exchange charge of PDBT-3DTh remained 78.3% after 100 cycles and 63.8% after 300 cycles, while PDBF-3DTh remained about 88.8% and 68.5% of electrochemical activity after 100 and 300 cycles (Table 3). In contrast, the stability of PDBT-EDOT and PDBF-EDOT remained 83.76% and 88.47% after 100 cycles,¹¹ better than PDBT-3DTh and PDBF-3DTh, which can be ascribed to the good stability of EDOT. Similar to 3-HexTh/3-MeTh end-capped polymers¹² in the long-term

switching stability, both polymers displayed better stability than those of thiophene-substituted polymers. Meanwhile, DBF as inner unit polymers exhibited better stability than DBT-based polymers, attributing to better conjugation of the polymer backbone.

Thermal Analysis

To investigate the thermal stability of PDBT-3DTh and PDBF-3DTh films, thermogravimetric analytical experiment (TGA) was performed under a nitrogen stream at a heating rate of 10 K min⁻¹, as shown in Supporting Information Figure S9. PDBF-3DTh shows slightly higher thermal stability over PDBT-3DTh. Both polymers initially underwent weight decrease about 3.6% for PDBT-3DTh and 6.5% for PDBF-3DTh at relatively low temperature (from 293 K to 350 K), which may be attributed to water evaporation according to many authors.²⁹ It means that the onset decomposition temperatures of PDBT-3DTh and PDBF-3DTh are at 324 K and 350 K, respectively. When the temperature increased up to about 1100 K, the residue of PDBT-3DTh and PDBF-3DTh were about 45% and 48%, respectively. The similar thermogravimetric degradation curves were exhibited for PDBT-3HexTh and PDBF-3HexTh.¹² However, under similar conditions, PDBT-Th and PDBF-Th¹² exhibited better thermal stability. To be specific, because of alkyl chain, PDBT-3DTh and PDBF-3DTh were easily to crack while thiophene-substituted polymers need higher temperature to decompose the skeletal backbone chain structure.

Morphology

Scanning electron micrographs (SEM) of polymers provide their clear surface and bulk morphologies, which are two important aspects closely related to their optical and electrical properties, such as charge transport and counterions storage capability.³⁰ The surface morphology of PDBT-3DTh and PDBF-3DTh deposited on the ITO electrode was investigated by SEM, as shown in Supporting Information Figure S10. PDBT-3DTh (A) and PDBF-3DTh (B) films exhibited smooth and compact morphology at high magnifications, which was beneficial to increase the electron transfer capability of conjugated polymer.²⁶ Also, the smooth and compact morphology of the polymers films were especially significant in the fabrication of electrochromic devices. The smooth surface of both polymer films were similar to P(DBT-EDOT) and P(DBF-EDOT),¹¹ while thiophene end-capped polymers¹² showed a lot of holes with different diameters. These differences were due to the different end units.

Spectroelectrochemistry

Spectroelectrochemical properties of the polymers (Fig. 7) were investigated in CH_3CN - Bu_4NPF_6 (0.1 mol L^{-1}) solvent and UV-Vis-NIR spectra were recorded upon external bias. Electrochemically produced polymer films on ITO were reduced to their neutral states at -0.5 V potential to remove any trapped charge and dopant ion before spectroelectrochemical analysis.

The electronic absorption spectra of neutral form of the films illustrate an absorption band at around 325 nm, which are attributed to the transitions from the thiophene-based



TABLE 3 (Optical and	Electrochemical	Properties	of Polymers
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	Electrochemistry and Linear Fitting				Redox Stability		Absorption		
Polymers	$E_{\rm ox,peak}$ (V)	$E_{\rm red,peak}$ (V)	$R_{\rm an}^2$	$R_{\rm cat}^2$	100th	300th	λ_{onset} (nm)	λ_{\max} (nm)	$E_{\rm g,opt}$ (eV)
PDBT-3DTh	0.92	0.88	0.997	0.999	78.3%	63.8%	440	353	2.82
PDBF-3DTh	1.10	0.90	0.998	0.997	88.8%	68.8%	430	329	2.72

valence band to its antibongding band, are mainly absorbing in the UV-region, with minor tailing into the visible region.³¹ The band gaps of PDBT-3DTh and PDBF-3DTh were calculated to be 2.82 eV and 2.72 eV through the onset of the π - π * transition. Compared with its analogs such as PDBT-Th ($E_g = 2.53$ eV), PDBF-Th ($E_g = 2.43$ eV), PDBT-3MeTh ($E_g =$ 2.63 eV), PDBF-3MeTh ($E_g = 2.46$ eV), PDBT-3HexTh ($E_g =$ 2.89 eV), and PDBF-3HexTh ($E_g = 2.75$ eV), we found that due to enhanced interchain packing of polymer chains caused by alkyl substituents on thiophene rings and raising



FIGURE 7 Spectroelectrochemistry of PDBT-3DTh (between 1.00 V and 1.55 V, $\Delta E = 0.05$ V) and PDBF-3DTh (between 1.0 V and 1.4 V, $\Delta E = 0.05$ V) on the ITO coated glass in MeCN-Bu₄NPF₆(0.1 mol L⁻¹). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

their subtle electronic changes on the conjugated block, the entire absorption spectra of DBT-3HexTh and DBF-3HexTh are redshifted compared with all the 3-HexTh/3-MeTh endcapped polymers.¹² In agreement with their results on electropolymerization behavior, the absorption spectra of 3-DTh end-capped polymers stayed slightly blueshift compared with those of 3HexTh end-capped polymers due to the increased strain of the longer dodecyl group (decreased orbital overlap and conjugation). Furthermore, the entire absorption bands of DBF-based polymers except for PDBF-3DTh shifted to the lower energy region compared with DBT-based polymers. As a consequence, a band gap reduction was observed for DBF-based polymers owing to the substitution of oxygen atom compared with DBT-based polymers (sulfur atom).

Upon the oxidation process of the polymer films, the absorptions in the UV-region started to decrease and new bands were intensified due to the formation of lower energy charge carriers such as polarons and bipolarons on the polymer backbone in the visible-region and near-IR-region. In the case of PDBT-3DTh, as the valence-conduction band at 350 nm diminished, a new band started to intensify at about 575 nm, accompanied with a new broad band around 1050 nm, which were due to the formation of lower energy charge carriers on the polymer backbone, along with a color change. Furthermore, both spectra recorded during potential cycling at 1.00 V to 1.55 V for PDBT-3DTh and 1.0 V to 1.4 V for PDBF-3DTh passed through clear isosbestic points at

TABLE 4 Colorimetric Data for Synthesized Polymers. [Color

 figure can be viewed in the online issue, which is available at

 wileyonlinelibrary.com.]

Polymers	CI	E Color Co	ordinates	Colors of Polymers		
		Neutral	Oxidized	Neutral	Oxidized	
PDBT-3DTh	L*	79.0822	48.2419			
	a*	2.9496	7.6619			
	b*	2.5041	-17.2970			
PDBF-3DTh	L*	83.2266	71.3795			
	a*	1.5351	2.3060			
	b*	7.0708	-1.7633			

TABLE 5 Electrochromic Parameters of the Polymers at Different Wavelengths

	Wavelength	Response time (s)			CE	
Sample	(nm)	ΔT	Oxidation	Reduction	$(cm^2 C^{-1})$	
PDBT- 3DTh	350	10.53%	8.6	9.6	171	
	575	25.23%	7.4	8.8	197	
	1050	16.11%	8.6	9.2	136	
PDBF- 3DTh	325	4.59%	8.2	8.4	87	
	550	8.69%	6.6	9.0	93	
	950	5.94%	6.6	8.8	78	

around 410 nm, indicating both polymer films being interconverted between their neutral and oxidized states.

To determine the color change, the CIE 1976 (L*, a*, b*) color space and photographs of the polymers were determined, in which L* is the parameter of the lightness, a* is the red-green balance and b* is yellow-blue balance $(-a^* \text{ and } +a^* \text{ correspond to green and red, while } -b^* \text{ and } +b^* \text{ correspond to blue and yellow, respectively}.³² The colorimetric data with a D65 illuminant as detailed for synthesized polymers are given in Table 4. Globally, fully oxidized state polymer films on one piece of ITO-coated glass were easy to obtain, and both polymers illustrated similar colors (blue in the oxidized state and light gray in the neutral state), which were similar to PDBT-3HexTh and PDBF-3HexTh.¹² The color would relate to the alkyl chain of thiophene, since the EDOT and thiophene end-capped polymers exhibited yellow in the neutral state.^{11,12}$

Electrochromic Switching Studies

Optical contrast (or percent transmittance, refers to the percentage transmittance change ($\Delta T\%$) at a specified wavelength), switching time (or response time, defined as the necessary time for 95% of the full optical switch), and coloration efficiency (CE) are very important parameters to evaluate electrochromic materials. They were analyzed by changes that occurred in the transmittance while switching the potential step wisely between the neutral state and oxidized state with a residence time of 10 s. Electrochromic parameters of the polymer films were summarized in Table 5.

It is clearly seen from the transmittance curves in Supporting Information Figure S11 that PDBF-3DTh displayed substandard optical contrast ratios. However, the obtained polymer PDBT-3DTh showed superior optical contrast compared with PDBF-3DTh, the optical contrast of which at 575 nm was found to be 25.23% with the highest CE value of 196.32 cm² C⁻¹. However, these obtained polymers exhibited slow response time in the oxidation and reduction processes, owing to the ionic conductivity of the electrolyte, accessibility of the ions to the electroactive sites (ion diffusion in thin films), magnitude of the applied potential, film thickness, and morphology of the thin film. $^{\rm 26}$

Deeply, for all the 3-alkylthiophenes end-capped DBT/DBF hybrid electrochromic polymers, DBT as inner unit based electrochromic polymers displayed higher optical contrast ratio, faster response time, and higher CE compared with DBF-based polymers. We ascribed this phenomenon to the reason that low onset oxidation potential for DBT based monomers make it reality to obtain better polymer films at relatively low potentials. Further, 3-MeTh/3-HexTh end-capped polymers exhibited better electrochromic properties, mainly attributed to the electron-donating effect of longer alkyl chain. Howeve, due to the introduction of dodecyl group on the thiophene ring, 3-DTh end-capped DBT/DBF polymers displayed commonly electrochromic properties because of decreasing the co-planarity and conjugation of aromatic systems.

Optical memory, one of the most important characteristics of electrochromic materials was monitored at 1050 nm as a function of time at -1.0 V and 1.4 V by applying the potential for 2 s for each 100 s time interval. As depicted in Supporting Information Figure S12, both polymer films in yellow colored state showed a true permanent memory effect since there was a little transmittance change under the applied potential (-1.0 V). In purple colored state, the polymers were rather less stable in terms of color persistence, which is probably due to the dopants reinclusion into the films and make the films partly doped.

CONCLUSIONS

In summary, the synthesis and electrochemical polymerization of DBT-3DTh and DBF-3DTh were comprehensively reported. As-formed polymers PDBT-3DTh and PDBF-3DTh were studied by cyclic voltammetry, UV-Vis, fluorescence, morphology, and thermogravimetric analysis. Further, their spectroelectrochemistry and electrochromism were also systematically investigated. PDBF-3DTh exhibited better redox stability and higher decomposition temperature than PDBT-3DTh. Reversely, PDBT-3DTh possessed lower optical band gap of 2.82 eV compared with PDBF-3DTh (2.72 eV). Spectroelectrochemistry displayed that both polymers were blue to light gray electrochromic polymers. The maximal contrast for PDBT-3DTh was measured to be 25.23% at 575 nm with the highest CE of 196 cm^2 C⁻¹. Due to the introduction of dodecyl group on the thiophene ring, 3-dodecylthiophenelinked DBT/DBF polymers displayed commonly electrochromic properties becauese of decreasing the planarity and conjugation of aromatic systems.

DBT/DBF-heterocycle hybrid electrochromic polymers have been reported continuously in our lab. The heteroatom substitution in similar systems can affect the electrochemical and optoelectronic properties of conjugated structures. DBT-based systems are electron richer than DBF-based systems, as a result, DBT-based conjugated polymers showed better electrochemical and electrochromic performances than DBF-based conjugated polymers due to the lower electronegativity, larger



atomic size and more polarizability of sulfur atom than oxygen atom. Moreover, substituents on the end units affect the performance not only through modulating the electronic nature but also by changing steric hindrance. Therefore, there is still an ongoing dynamic and further research on electrochromism in respect of tuning the backbone structure and alkyl side chains.

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